

AFIT/GEE/ENV/00M-04

MODELING THE EFFECT OF NONLINEAR AND
RATE-LIMITED SORPTION ON THE
NATURAL ATTENUATION OF
CHLORINATED ETHENES

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AFIT/GEE/ENV/00M-04

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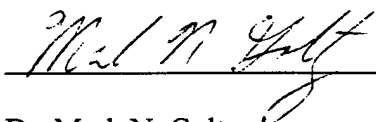
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Peter P. Feng

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Abstract

Chlorinated solvents like tetrachloroethene (PCE) and trichloroethene (TCE) are the most common detected groundwater contaminants at Department of Defense installations in the United States. Unfortunately, technologies conventionally used to remediate chlorinated solvent-contaminated groundwater often fall short of achieving regulatory goals. Natural attenuation of chlorinated solvents offers an alternative remediation strategy that may achieve goals. However, the processes involved with natural attenuation are not fully understood, and this lack of understanding has hindered acceptance of natural attenuation by regulatory agencies.

This study involved use of a numerical model that incorporated the physical, chemical, and biological processes thought to be relevant to the fate and transport of chlorinated ethenes in the subsurface. The model was used to conduct a parameter sensitivity analysis, to investigate the effect of non-linear and rate-limited sorption processes on the natural attenuation of chlorinated ethenes. The model showed that both rate-limited and non-linear sorption resulted in early arrival of contaminant at wells downgradient of a source area, as well as persistence of contamination at the wells for long periods of time.

MODELING THE EFFECT OF NONLINEAR AND RATE-LIMITED SORPTION ON THE NATURAL ATTENUATION OF CHLORINATED ETHENES

1.0 Introduction

1.1 Motivation

The use of chlorinated solvents in the United States began in 1906 and increased rapidly following World War II (Pankow and Cherry, 1996). Carbon tetrachloride, chlorobenzene, chloroform, dichloromethane, tetrachloroethylene (PCE) and trichloroethylene (TCE) are all commonly used chlorinated solvents. This research will focus on the chlorinated ethenes, PCE and TCE. The production of PCE and TCE started in 1923. Both compounds are currently used as chemical intermediates, dry cleaning additives and metal degreasers (Pankow and Cherry, 1996). PCE and TCE are classified as dense non-aqueous phase liquids (DNAPL). When spilled in the subsurface environment a DNAPL, because it is denser than water, seeps below the water table as a separate phase. This separate phase of contaminant slowly dissolves into passing groundwater. Because of the relatively low solubility of PCE and TCE in water, a DNAPL source area can persist for decades (Pankow and Cherry, 1996).

PCE and TCE groundwater contamination is a significant national, DOD and Air Force problem. For example, the USEPA found that PCE and TCE were two of the three most commonly detected organic compounds in a survey of 945 groundwater based drinking water supplies (Westrick et al., 1984). TCE has been found at 852 and PCE at 771 of the 1430 NPL sites as of September 1997 (USEPA, 1998). The Air Force was a wide user of PCE and TCE and over 70% of Air Force installations have groundwater contaminated with either PCE or TCE (Thiele, personal communication, 1999).

PCE and TCE and over 70% of Air Force installations have groundwater contaminated with either PCE or TCE (Thiele, personal communication, 1999).

Currently, there is no technology that has been proven to remediate PCE or TCE DNAPL source areas, though research is underway (Pankow and Cherry, 1996). Thus, PCE and TCE in the dissolved phase must be dealt with. The most common technology used to remediate chlorinated solvent plumes is conventional pump and treat. This remediation strategy calls for pumping the contaminated water out of the ground and treating it to remove or destroy the contaminant. However, because of the relatively low solubility of PCE and TCE in groundwater, and the relatively large mass of contaminant that may be present in the source area, pump and treat strategies may take many decades to remove significant amounts of contaminant (NRC, 1994). Pump and treat has been shown to be a useful containment technology; for example, a line of pumps down gradient of a contaminant plume can prevent the plume from moving to areas where it will present a risk. Unfortunately, pump and treat is a relatively expensive containment technology, requiring operation and maintenance of the system over decades (Pankow and Cherry, 1996). Other containment technologies that are being considered involve the use of passive barriers. One such passive barrier that has recently been implemented involves emplacement of zero-valent iron in a trench (Tratnyek, 1996). As groundwater that has been contaminated by chlorinated ethenes flows through the trench, the contaminants are reductively dechlorinated. This technology has been successfully implemented at various sites (Thomas et al., 1995). The main advantage to the reactive barrier is the cost of implementation. The implementation simply requires the placement of iron filings in a

trench that intercepts the groundwater. Iron filings are widely available, inexpensive, and there is no need for active pumping. There are two main disadvantages to reactive barriers. Reactive barriers are limited to how deep the trench can be placed and therefore mainly deal with relatively shallow contamination. In addition, since the barrier is passive, seasonal changes in groundwater flow may allow the contaminant to bypass the trench.

A third containment strategy involves the use of natural attenuation. The United States Environmental Protection Agency defines monitored natural attenuation as follows:

The term "monitored natural attenuation," as used in this Directive, refers to the reliance on natural attenuation processes (within the context of a carefully controlled and monitored clean-up approach) to achieve site-specific remedial objectives within a time frame that is reasonable compared to other methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. These in-situ processes include, biodegradation, dispersion, dilution, sorption, volatilization, and chemical or biological stabilization, transformation, or destruction of contaminants (OSWER Directive 9200.4-17, 1997).

Today monitored natural attenuation is widely accepted as a remedy to control hydrocarbon contamination plumes. However, the EPA's view on monitored natural attenuation for chlorinated solvents is that "the hydrologic and geochemical conditions favoring significant biodegradation of chlorinated solvents sufficient to achieve remediation objectives within a reasonable timeframe are anticipated to occur only in limited circumstances" (OSWER Directive 9200.4-17, 1997). In the OSWER directive, however, the EPA notes that "recent research has been useful in furthering our understanding of natural attenuation processes for chlorinated compounds" (OSWER, 1997). Thus, as our understanding of these processes increases, we become better able to

apply monitored natural attenuation to remedy chlorinated solvent contamination when it is appropriate. The main advantage to monitored natural attenuation is the cost. If it can be shown that the degradation of chlorinated solvents occurs naturally there is no need for active pump and treat strategies. The main cost when applying monitored natural attenuation is the cost of monitoring the site. The disadvantage to monitored natural attenuation is that the naturally occurring processes may not be fast enough to be protective of health and the environment. Another disadvantage of natural attenuation is its perception by the public as a "do nothing" option. A better understanding of the fate of chlorinated solvents in the subsurface will help us to address these concerns and apply the strategy of monitored natural attenuation in a manner that assures the remedy will be protective of human health and the environment.

One of the processes that impacts the fate of dissolved chlorinated ethenes in the subsurface is sorption to aquifer solids. It is believed that biodegradation of these compounds does not occur when they are sorbed, as the chemicals are not accessible to the bacteria that metabolize them (Mihelcic and Luthy, 1991). Thus, sorption could play an important role in the natural attenuation process. It is typically assumed that sorption can be modeled as a linear equilibrium process (Veerkamp, 1999; Aziz et al, 1999; Carey et al, 1999). This assumption of linear, equilibrium sorption may lead to non-conservative results when modeling natural attenuation. Numerous studies have shown that "non-ideal" sorption (that is, nonequilibrium, nonlinear, and/or non-singular sorption) may affect contaminant transport in the subsurface (Crittenden et al., 1986; Brusseau and Rao, 1989; Jepsen and Lick, 1999; Heyse et al., 1999). Accounting for

nonlinearity and sorption kinetics in a model may be important in our attempt to understand natural attenuation of chlorinated ethenes in groundwater.

The proposed work will incorporate the effects of non-linear and/or rate limited sorption into a model of natural attenuation of PCE and TCE, so that the impact of non-ideal sorption on the natural attenuation process can be simulated. This computer model will allow a better understanding of what processes might be at work in the subsurface environment and how those processes may impact the ultimate fate of the contaminants.

1.2 Research Objectives

1. Develop a package that incorporates non-linear or rate-limited sorption into a model of the relevant biodegradation processes that impact chlorinated solvents.
2. A sensitivity analysis will be performed on the variables used in sorption/desorption scenarios

1.3 Definition of Terms

Abiotic – Process which occurs without the presence of living organisms

Advection – Flow of molecules traveling at the average velocity of the groundwater

Aerobic – Environmental conditions where oxygen is present.

Anthropogenic – Man-made (Wiedemeier et al., 1998)

Bacteria – Members of a group of diverse and ubiquitous prokaryotic (i.e. cells lacking a nucleus), single-celled organisms (Atlas and Bartha, 1993).

Biodegradation – Process where bacteria mineralize or transform contaminants using organic contaminants as an energy source (Domenico and Schwartz, 1998)

Biotic – Processes which occur in the presence of living organisms

Chlorinated Solvent – Hydrocarbon in which chlorine atoms are in place of one or more hydrogen atoms in the structure of the compound

Cometabolism – The process in which a compound is fortuitously degraded by an enzyme or cofactor produced during microbial metabolism of another compound (Wiedemeier et al., 1998)

Daughter Product – A compound that results directly from the biodegradation of another. For example cis-1,2-dichloroethene (cis-1,2-DCE) is commonly a daughter product of trichloroethene (TCE). (Wiedemeier et al., 1998)

Dechlorination – Removal of chlorine atoms from a compound

Desorption – Release of chemicals that are attached to a solid

Diffusion – Process in which molecules flow from high concentrations to low concentrations

Dispersion – The spreading of molecules due to the tortuous pathways located within the aquifer

Electron Acceptor – A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases the chlorinated aliphatic hydrocarbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride. (Weidemeier et al, 1998)

Electron Donor – A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon. (Weidemeier et al., 1998)

Microorganism – An organism of microscopic scale capable of reproduction and growth on primary substrates (NRC, 1994)

Methanogenesis – The process of creating methane from H_2 and CO_2 during the respiration of methanogens (Atlas and Bartha, 1993)

Mineralization – The conversion of an organic compound to its inorganic constituents

Monooxygenase – A microbial enzyme that catalyzes reactions in which one atom of the oxygen molecule is incorporated into a product and the other atom appears in water.

(Weidemeier et al., 1998)

Natural Attenuation – Natural processes that occur that can destroy or alter chemicals in the groundwater

Oxidation – Loss of electrons from a compound, such as an organic contaminant.

Primary Substrates – The electron donor and electron acceptor that are essential to growth and reproduction of microorganisms (NRC, 1994)

Reduction – Gain of electrons from a compound. It occurs when another compound is oxidized.

Reductive Dechlorination – Removal of chlorine atoms and replacement with hydrogen atoms.

Sorption – Adherence of a substance to a solid through either chemical or physical processes. Sorption can be linear, nonlinear, and rate-limited.

Substrate – A compound that microorganisms can use in the chemical reactions catalyzed by their enzymes

Transmissivity – The volume of water flowing through one face of a prism in a unit time under a unit hydraulic gradient. (Domenico and Schwartz, 1998)

2.0 Literature Review

2.1 Overview

This literature review will cover four major areas. First, the physical and chemical processes that affect the fate of dissolved contaminants in groundwater will be described. Second, the biological processes relevant to natural attenuation of chlorinated ethenes will be explained. Third, past research on the evidence of natural attenuation of chlorinated ethenes at contaminated groundwater sites will be explored. Finally, as computer modeling has been used to better understand the processes at work in the subsurface, a discussion of groundwater fate and transport modeling focusing on models that incorporate the transport mechanisms relevant to the natural attenuation of chlorinated ethenes will follow.

2.2 Physical/Chemical Transport

The general equation governing the transport of contaminants in groundwater is (Miller and Weber, 1984):

$$\frac{dC}{dt} = \left[v_x \frac{dC}{dx} \right] + \left[D_x \frac{d^2C}{dx^2} \right] + \left[D_y \frac{d^2C}{dy^2} \right] + \left[D_z \frac{d^2C}{dz^2} \right] - \left[\frac{dS}{dt} \frac{\rho}{n} \right] \pm r \quad (2.1)$$

where

C = concentration of contaminant in aqueous phase $[M/L^3]$

t = time $[T]$

v_x = average linear velocity of groundwater in the x-direction $[L/T]$

D_x, D_y, D_z = dispersion coefficients in the x, y, and z-directions, respectively $[L^2/T]$

r = source/sink term of contaminant production/destruction in aqueous phase $[M/L^3-T]$

S = sorbed mass of solute per mass of aquifer solid [M contaminant/M solids]

ρ = bulk density of aquifer solids [M/L³]

n = porosity of aquifer material [-]

Equation 2.1 is a mass balance expression for a contaminant in the aqueous phase. The first term on the right hand side represents transport of contaminant in the x-direction by advection. The second, third, and fourth terms on the right hand side represent dispersion in the x, y, and z-direction respectively. The fifth term on the right hand side represents removal of contaminant from the aqueous phase by sorption onto aquifer solids. The last term on the right hand side is a source/sink term, representing production or removal of contaminant from the aqueous phase due to a chemical biological, or nuclear decay reaction. In the following sections, we will discuss the physical/chemical processes represented by the first five terms on the right hand side of equation 2.1 in more detail. In section 2.3 we will discuss biological processes relevant to the natural attenuation of chlorinated ethenes, which are represented by the reaction term (r) in equation 2.1.

2.2.1 Advection

Advection is typically the primary mechanism for the transport of dissolved solutes in groundwater. The transport is due to the bulk flow of the water, which is determined by the average linear velocity of the flowing groundwater. The average linear velocity of a fluid flowing in a porous medium is determined using Darcy's Law (Domenico and Schwartz, 1998).

$$v = \frac{K * i}{n} \quad (2.2)$$

where:

K = the hydraulic conductivity of the porous medium [L/T]

i = the gradient of hydraulic head of the groundwater [-]

n = porosity of aquifer material [-]

In Darcy's equation, porosity and hydraulic conductivity are both properties of the porous medium. Hydraulic heads, and the hydraulic head gradient, may be determined by solving the equations of flow, with appropriate initial and boundary conditions (Domenico and Schwartz, 1998).

2.2.2 Dispersion

Dispersion is the spreading of mass beyond the region that would be caused by advection alone. There are two processes that lead to dispersion, diffusion and mechanical dispersion (Domenico and Schwartz, 1998). Molecular diffusion is the movement of molecules from areas of high concentration to areas of low concentration. Molecular diffusion is only important at extremely low flow velocities and is usually ignored in groundwater calculations (Clark, 1996). Mechanical dispersion represents the spreading of contaminant molecules due to spatial variation of groundwater flow velocity. Hence, contaminant molecules being carried along with the flow by advection do not necessarily move at the groundwater average linear velocity. In actuality the individual molecules flow faster and slower than the average linear velocity due to the tortuosity of the porous medium and the parabolic distribution of groundwater velocities within pores.

Mechanical dispersion also accounts for the heterogeneity of the porous medium, where some groundwater may be flowing relatively fast through high hydraulic conductivity regions and some flowing relatively slowly through low hydraulic conductivity regions.

Mechanical dispersion has been shown to be proportional to the average linear velocity, and can be modeled using the following equation (Clark, 1996).

$$D_i = \alpha_i * v_x \quad (2.3)$$

Where

D_i = dispersion coefficient in the i^{th} direction [L^2/T]

α_i = dispersivity in the i^{th} -direction [L]

v_x = average linear velocity of groundwater in the x-direction [L/T]

2.2.3 Sorption

Sorption is the process where an absorbate binds to an absorbent. In this research, the absorbate is the chlorinated solvent contaminant and the absorbent is the solids located within the subsurface. Sorption can be characterized as either an equilibrium or rate-limited phenomenon. Equilibrium sorption can be modeled as a linear or non-linear process. Equilibrium sorption may be assumed when the flow of groundwater and other processes affecting contaminant transport are slow compared to the rate of sorption. In this event the sorption of the contaminant can be considered instantaneous. In many circumstances, however, the assumption of equilibrium sorption is inappropriate. One significant study that was conducted at the Canadian Air Force Base in Borden, Ontario, found that the equilibrium assumption was inadequate to describe the subsurface transport of five sorbing compounds. The nonideal transport was attributed to rate-limited sorption/mass transfer (Robert et al., 1986; Goltz and Roberts, 1988; Quinodoz and Valocchi, 1993; Cvetkovic and Dagan, 1994; Thorbjarnarson and Mackay, 1994).

Rate-limited sorption can have a significant affect on the biodegradation of chlorinated solvents. The biomass is present in the aqueous phase and degradation can only occur in that phase. If the chlorinated solvent slowly desorbs into the aqueous phase then the rate at which degradation can occur will depend upon the desorption rate (Fu et al., 1994; Fry and Istok, 1994). There are many ways of modeling rate-limited sorption but the two most common are to assume sorption kinetics can be described as either a first-order process or a diffusion-controlled process. Rate-limited sorption should be assumed when sorption is slow relative to the other processes affecting contaminant transport.

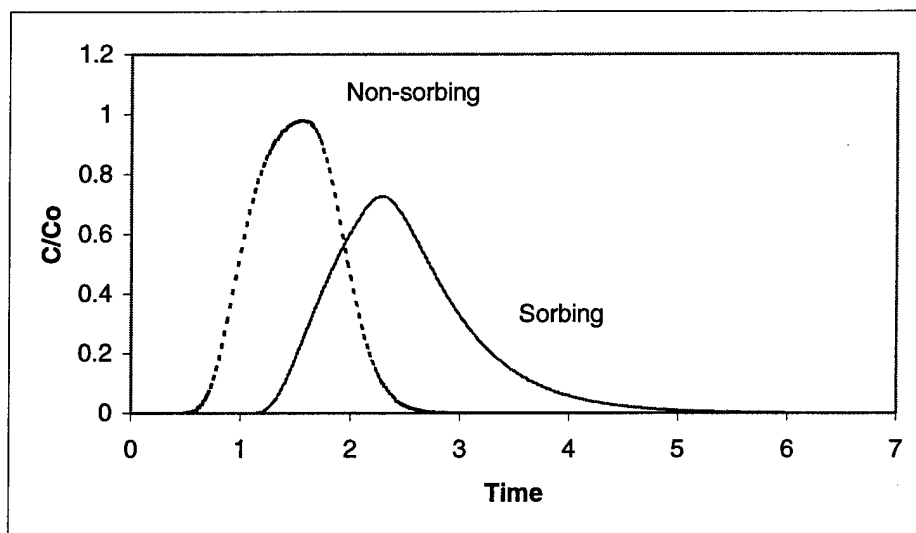


Figure 2.1 Breakthrough Curve

A breakthrough curve can show the effect of sorption on contaminant transport. A breakthrough curve is a plot of contaminant concentration versus time at a point. Shown in Figure 2.1 are breakthrough curves of two contaminants. One contaminant is conservative (non-sorbing) while the other sorbs. Note that transport of the sorbing contaminant is retarded. This is because while the non-sorbing contaminant is being transported by the flowing groundwater, a portion of the sorbing contaminant is immobile, as it's sorbed to the aquifer solids. It is thus important, when modeling

contaminant transport, to know the relative concentration of contaminant in the sorbed and aqueous phases. If we assume equilibrium sorption, the relative concentrations of contaminant in the sorbed and aqueous phases can be modeled and predicted using a sorption isotherm. A sorption isotherm describes the relationship between contaminant in the sorbed and aqueous phases.

2.2.3.1 Equilibrium Sorption

2.2.3.1.1 Linear Model

Linear equilibrium sorption assumes that the binding of contaminants to aquifer solids is instantaneous and that the concentration of sorbed contaminant is directly proportional to the concentration of the dissolved contaminant (Figure 2.2).

This can be modeled by (Srinivasan and Mercer, 1988):

$$S = K_d * C \quad (2.4)$$

Where

S = sorbed concentration [M contaminant/M solids]

K_d = sorption distribution coefficient [L^3/M]

C = dissolved contaminant concentration in the groundwater [M/L^3]

Note that if linear equilibrium sorption is assumed, the dS/dt term in equation (2.1) can be replaced by dC/dt multiplied by a constant ($K_d\rho/n$). Equation (2.1) can then be simplified and rewritten by dividing all terms by a retardation factor, R , where $R = 1 + K_d\rho/n$.

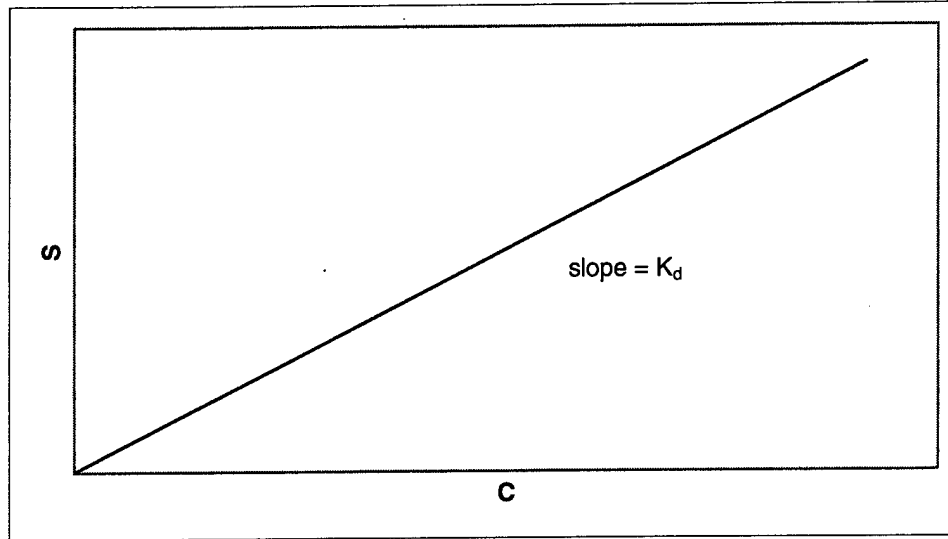


Figure 2.2 Linear Sorption Isotherm

2.2.3.1.2 Nonlinear Model

Unlike the linear model (Figure 2.2), the nonlinear model does not assume that sorbed concentrations are directly proportional to aqueous concentrations (Figure 2.3). While linear sorption is a good assumption when aqueous contaminant concentrations are relatively low, it may be necessary to use the nonlinear model when concentrations vary over a large range (Brusseau, 1998).

Nonlinear sorption has been modeled using the Freundlich isotherm (Schlebaum et al., 1999).

$$S = K_f * C^n \quad (2.5)$$

Where

S = sorbed concentration [M contaminant/M solids]

K_f = Freundlich adsorption constant $[(M/L^3)^{-n}]$

C = dissolved concentration of the contaminant in groundwater $[M/L^3]$

n = Freundlich exponent $[-]$

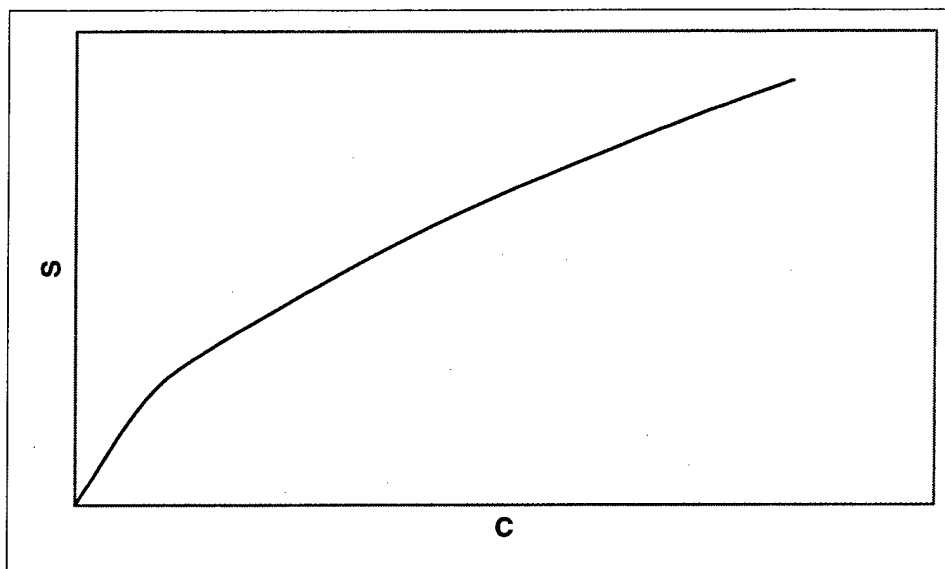


Figure 2.3 Non-linear Sorption Isotherm

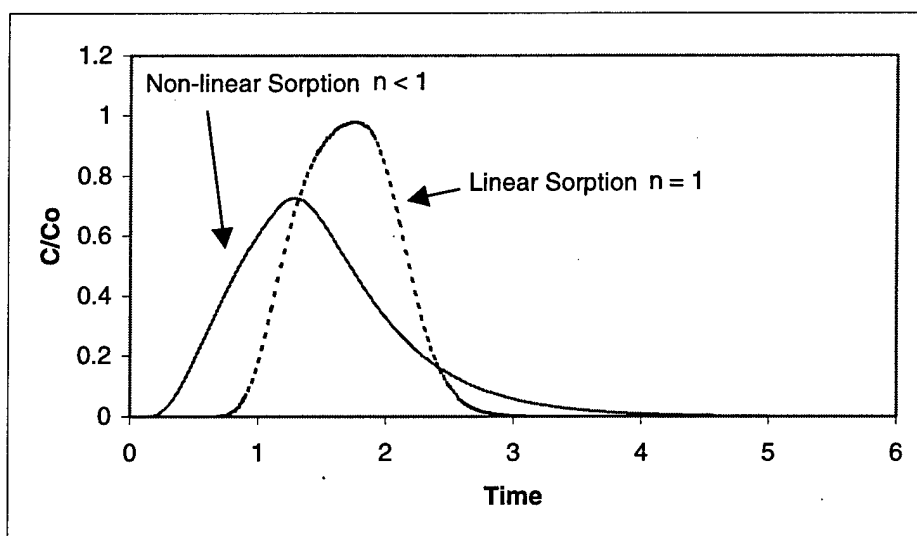


Figure 2.4 Non-linear vs. Linear Breakthrough Curves

The effect of nonlinear sorption on contaminant transport is illustrated in Figure 2.4. When the Freundlich exponent, n , is less than 1, which is typically the case, nonlinear sorption leads to the early breakthrough curve and contaminant concentration “tailing” shown in the Figure. Note, though, that this breakthrough curve asymmetry, which is

commonly observed, may also be due to soil heterogeneities and rate-limited sorption (Crittenden et al., 1986; Brusseau and Rao, 1989).

2.2.3.2 Rate-Limited Sorption

2.2.3.2.1 First-Order Model (Linear Equilibrium)

Most field-scale modeling studies of contaminant plumes make the local equilibrium assumption (LEA) (Clement et al., 1999; Aziz et al., 1999). The LEA is based on the premise that the interactions between the contaminant and the aquifer material are so rapid compared to advective residence times that it can be assumed that the interactions are instantaneous (Clark, 1996). When the sorption process occurs at a rate that is similar to the rate of advection, the LEA is not appropriate and rate-limited sorption must be accounted for. As noted earlier, there is considerable evidence from field studies and observations of asymmetric breakthrough curves (sharp breakthrough and tailing, similar to that seen in Figure 2.4) that the LEA is often inadequate to describe reality. Rate limited sorption can be modeled using the following first-order rate expression (Semprini and McCarty, 1992).

$$\frac{dS}{dt} = \alpha * (K_d C - S) \quad (2.6)$$

S = sorbed concentration [M contaminant/M solids]

K_d = sorption distribution coefficient [L^3/M]

α = first-order rate constant for mass transfer of contaminant between the aqueous and the solid phases [T^{-1}]

C = dissolved concentration of the contaminant in groundwater [M/L^3]

Note that when equilibrium is attained ($dS/dt = 0$) equation 2.6 reverts to the linear model (equation 2.4).

2.2.3.2.2 First-Order Model (Non-Linear Equilibrium)

Rate-limited sorption can also be modeled assuming a first-order rate coupled with a nonlinear equilibrium expression. If we assume a Freundlich isotherm and a first-order rate expression, we can use the following equation to model sorption kinetics.

$$\frac{dS}{dt} = \alpha * (K_f C^n - S) \quad (2.7)$$

S = sorbed concentration [M contaminant/M solids]

K_f = Freundlich adsorption constant $[(M/L^3)^{-n}]$

α = first-order rate constant for mass transfer of contaminant between the aqueous and the solid phases $[T^{-1}]$

C = dissolved concentration of the contaminant in groundwater $[M/L^3]$

n = Freundlich exponent $[-]$

Note that when equilibrium is attained ($dS/dt = 0$), equation 2.7 reverts to the Freundlich model (equation 2.5).

The relative effect of the mass transfer rate depends on the ratio of the mass transfer time constant ($1/\alpha$) and the advective time constant (RL/v) (Goltz and Oxley, 1991):

$$\frac{\left(\frac{1}{\alpha}\right)}{\left(\frac{R * L}{v}\right)} \quad (2.8)$$

where:

R is the retardation factor (defined in the text below Equation 2.4) [-]

L is the system length scale; for example, the distance from the source to a down gradient observation well [L]

v is the average linear velocity of the groundwater [L/T]

It was determined that rate-limited sorption has its largest effect when the ratio defined by equation 2.8 falls between 0.01 and 1.0 (Goltz and Oxley, 1991).

2.2.3.2.3 Diffusion Model

As noted earlier, diffusion is the process of contaminant transport from areas of high concentration to areas of low concentration. Rate-limited sorption due to diffusion may result from regions of immobile water adjacent to sorption sites so that sorption cannot occur until contaminant diffuses through the immobile water to the site. For example, Figure 2.5 schematically shows sorption sites in a low hydraulic conductivity lens. As contaminated water flows through high hydraulic conductivity regions adjacent to the lens (with contaminant transport affected by advection and dispersion), diffusion moves contaminant from the high hydraulic conductivity region (where concentrations are high) to the low conductivity region (where concentrations are low). Thus, sorption is rate-limited by the diffusive transport process. Diffusion may be modeled using Fick's Second Law of Diffusion (Clark, 1996). However, in past research, it was shown that Fickian diffusion can be modeled using a first-order approximation (Ball and Roberts, 1991; Goltz, 1986).

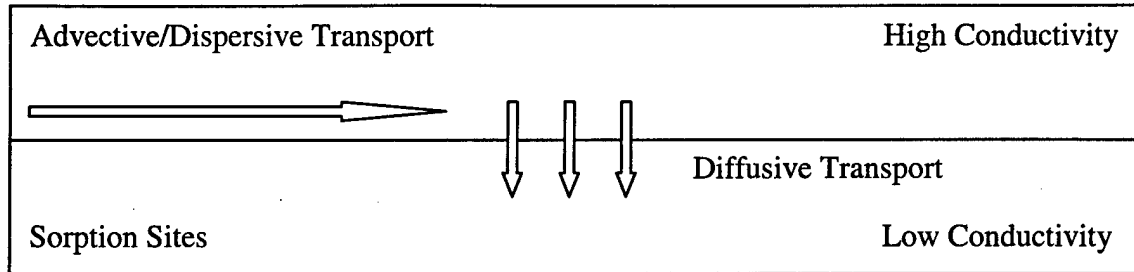


Figure 2.5 Diffusion Model

2.3 Biological Natural Attenuation Process

2.3.1 Anaerobic Processes

2.3.1.1 Reductive Dechlorination

Reductive dechlorination of halogenated ethenes can occur either through halorespiration or anaerobic cometabolism. In halorespiration, the microorganisms use the chlorinated compound as an electron acceptor (McCarty, 1997). In essence, the bacteria “breathe” the chlorinated compound, hence the term halorespiration. The electron donor in the reaction is some either natural or anthropogenic source of carbon. In anaerobic cometabolism, the degradation of the chlorinated solvent occurs fortuitously when the microorganisms oxidize a carbon source (the electron donor) using an electron acceptor other than oxygen (e.g. nitrate, manganese (IV), iron (III), sulfate, carbon dioxide). Table 2.1 lists the various electron acceptors in order of highest energy released to lowest energy released.

Table 2.1 Terminal Electron Acceptors, Microorganisms, and Energy

| Terminal Electron Acceptor | Common Organism | Oxidation state, marginal conditions, organisms, or activities | Process or Reduced End Product |
|--|------------------------|---|--|
| Oxygen | Aerobes | Aerobic Aerotolerant anaerobes | H ₂ O |
| Nitrate (NO ₃ ⁻) | Nitrate reducers | Anoxic conditions Facultative Anaerobes | N ₂ , Nitrite (NO ₂) |
| Manganese (Mn IV) | | Anaerobic | Mn(II) |
| Halogenated Organics (RX) | | Reductive dehalogenation by halorespiration | Dehalogenated Carbons (RH, X ⁻) |
| Iron (Fe III) | Iron reducers | | Fe (II) |
| Organics Molecules (CH ₂ O) | Fermentative organisms | Strict anaerobes | Alcohols, Fatty Acids, Ketones, H ₂ |
| Sulfate (SO ₄ ²⁻) | Sulfate reducers | Simultaneous reactions of fermentation, sulfate reduction, and methanogenesis | H ₂ S, HS ⁻ , S, S ₂ ⁻ |
| Carbon Dioxide (CO ₂) | Methanogens | | CH ₄ |

after Dean (1992) and Sawyer et al. (1994)

By either of these processes, the reductive dechlorination of tetrachloroethylene (PCE) produces trichloroethylene (TCE). TCE dechlorinates to produce dichloroethylene (DCE). Three isomers of DCE may exist: cis-1,2-DCE, trans-1,2-DCE, and 1,1-DCE, with cis-1,2-DCE the most predominant form produced by the reductive dehalogenation of TCE (Klier et.al., 1999). DCE then dechlorinates to vinyl chloride (VC) which finally

goes to ethene. Ethene, which is completely dehalogenated, is a desired end product for PCE and is not hazardous to human health. On the other hand, VC is a known carcinogen (Creech and Johnson, 1974; Maltoni and Lefemine, 1974). Unfortunately, in an anaerobic environment, the less chlorinated compounds are more difficult to reduce, so vinyl chloride degrades at extremely low rates (Freedman and Gossett, 1989). Figure 2.6 shows the reductive dechlorination pathway for the chlorinated ethenes.

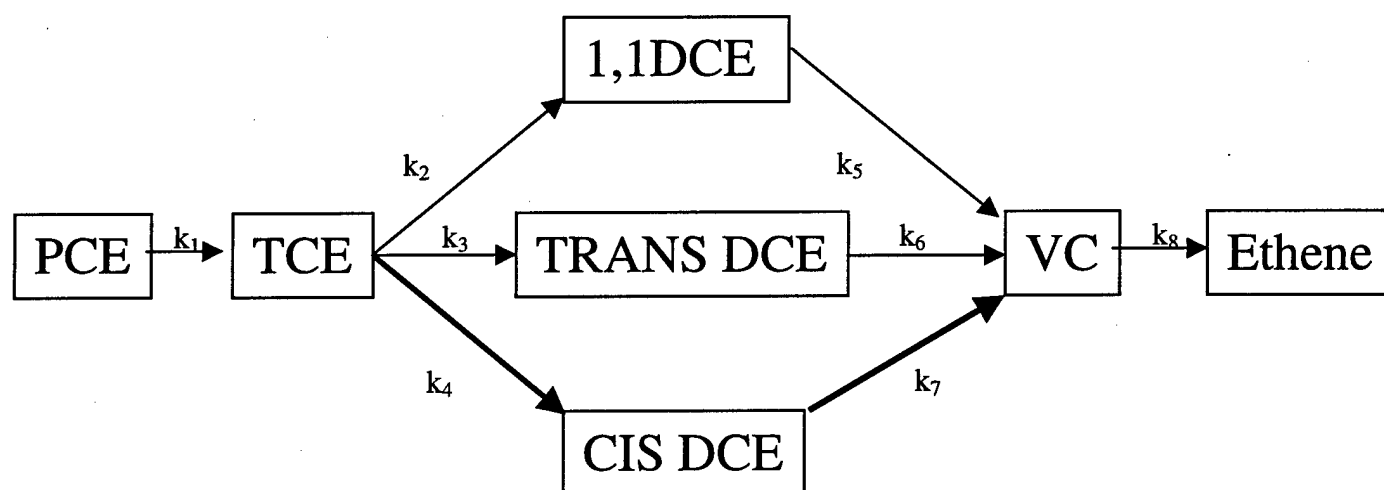


Figure 2.6 Reductive Dechlorination of PCE
(Freedman and Gossett, 1989)

It has been shown that each step in the reductive dechlorination pathway may be modeled as a first-order process so that the sink term, r , in equation 2.1 can be expressed as (Clement et. al., 1999):

$$r = -k_i C \quad (2.9)$$

where:

k_i = first-order reaction rate [T^{-1}]

C = dissolved contaminant concentration in the groundwater [M/L^3]

It has been shown that the k_i 's decrease with decreasing chlorination (Clement et al., 1999).

2.3.2 Aerobic Processes

2.3.2.1 Aerobic Cometabolism

Aerobic cometabolism occurs when microorganisms produce a nonspecific enzyme while metabolizing a food source, that is, a source of carbon and energy. In this work, we will focus on methanotrophs. Methanotrophs oxidize methane for energy and growth. The enzyme produced by the methanotrophs to oxidize methane is methane monooxygenase (MMO). Methane monooxygenase is nonspecific, and is also able to oxidize chlorinated compounds fortuitously, producing the chlorinated epoxide which is highly unstable (see Figure 2.7). The epoxide chemically decomposes to form carbon monoxide, glyoxylic acid, chlorinated acids and formic acids which can be easily biodegraded by other microorganisms present in the subsurface to ultimately produce carbon dioxide, water and chloride ions (Little et al., 1988). Aerobic cometabolism has been shown to be a mechanism applicable to the co-oxidation of TCE, DCE isomers, and VC but not PCE (Weidemeier et.al., 1999). It has also been shown that the less chlorinated compounds are more readily cometabolized aerobically (Semprini and McCarty, 1994).

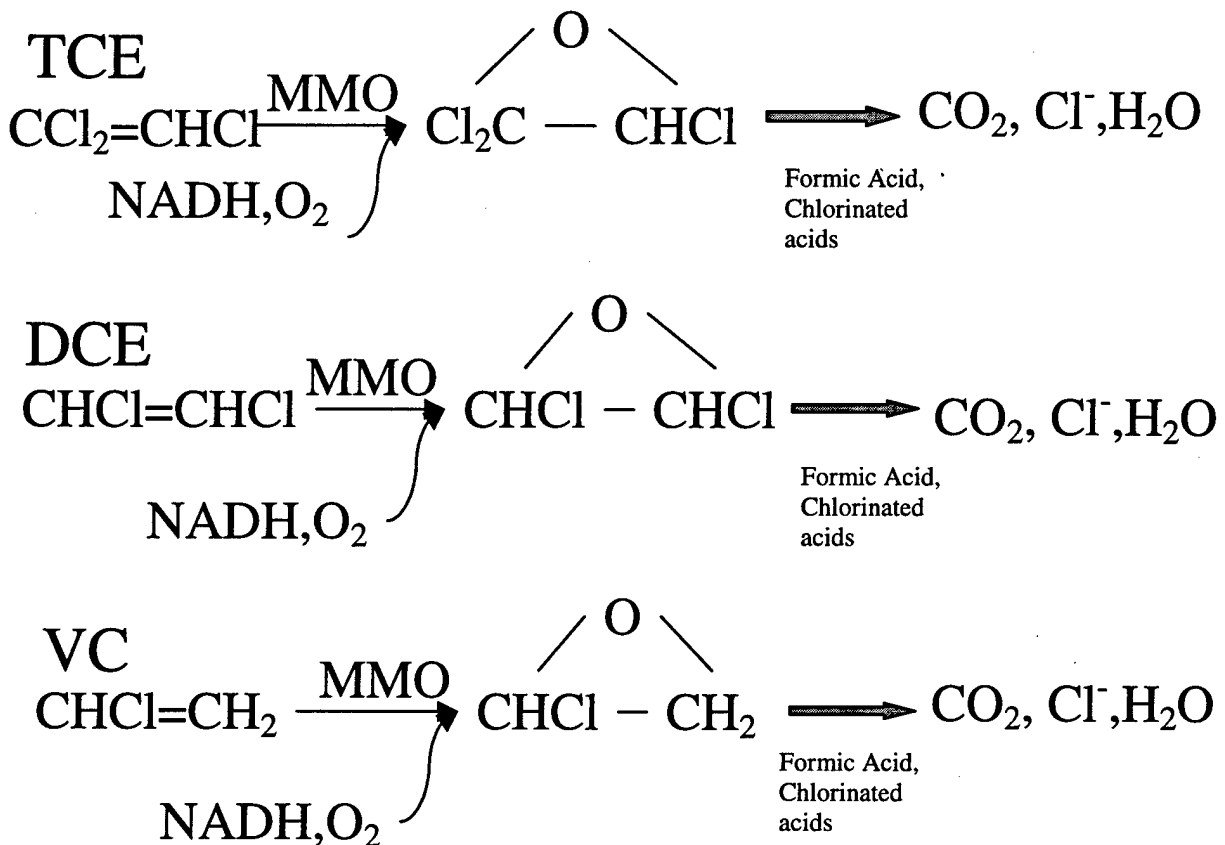


Figure 2.7 Aerobic Cometabolism
(Semprini and McCarty, 1994)

It has been shown that dual Monod kinetics can be used to model aerobic cometabolism (McCarty et al., 1984; Bouwer and McCarty, 1985), so the reaction term in equation 2.1 can be modeled as:

$$r = \frac{dC}{dt} = -X * k \left[\frac{C}{K_s + C} \right] * \left[\frac{C_a}{K_{s_a} + C_a} \right] \quad (2.10)$$

where:

$\frac{dC}{dt}$ is the change in concentration of the target contaminant over time $[\text{M/L}^3\text{-T}^{-1}]$

X is the concentration of bacteria active for cometabolic transformation $[\text{M/L}^3]$

k is the maximum utilization rate of cometabolism $[\text{M/M-T}^{-1}]$

C is the concentration of the target contaminant $[M/L^3]$

K_s is the half saturation constant of the target contaminant $[M/L^3]$

C_a is the concentration of the electron acceptor (that is oxygen) $[M/L^3]$

K_{s_a} is the half saturation constant of the electron acceptor $[M/L^3]$

In this dual Monod model, the rate of cometabolism is dependent on the concentrations of both the target contaminant and the electron acceptor (oxygen), as well as the concentration of active bacteria. It has also been seen that competitive inhibition may slow degradation of the chlorinated compound during aerobic cometabolism (Semprini and McCarty, 1992). Competitive inhibition occurs when the growth substrate (the methane) and the nongrowth substrate (the chlorinated compound) compete for the available active sites on the methane monooxygenase (Semprini and McCarty, 1992). This process can be modeled by modifying equation 2.10 as follows (Semprini and McCarty, 1992):

$$r = \frac{dC}{dt} = -X * k \left[\frac{C}{K_s + C + \frac{K_s * C_d}{K_{s_d}}} \right] * \frac{C_a}{K_{s_a} + C_a} \quad (2.11)$$

where:

K_{s_d} is the half saturation constant of the electron donor $[M/L^3]$

Because of the term $(K_s * C_d / K_{s_d})$ in the denominator, an increase in methane concentration leads to a decrease in the rate of cometabolism.

Equations 2.10 and 2.11 depend on the growth and decay of the aquifer bacteria as quantified in the parameter X . The bacteria growth and decay can be modeled using dual

Monod kinetics where bacterial growth/decay depends on the availability of electron donor (methane) and acceptor (oxygen) in accordance with the following expression (Semprini and McCarty, 1991).

$$\frac{dX}{dt} = X * k_1 * Y \left(\frac{C_d}{K_{sd} + C_d} \right) \left(\frac{C_a}{K_{sa} + C_a} \right) - b * X \left(\frac{C_a}{K_{sa} + C_a} \right) \quad (2.12)$$

where:

k_1 is the maximum utilization rate of the electron donor [M donor/M cells-day]

K_{sd} is the half saturation constant of the electron donor [M/L³]

Y is the yield coefficient [M cells/M donor]

b is the cell decay coefficient [T⁻¹]

C_d is the concentration of the electron donor (that is, methane) [M/L³]

Electron donor and acceptor utilization may be modeled using the two dual Monod expressions, below (Semprini and McCarty, 1991).

$$\frac{dC_d}{dt} = -k_1 * X \left(\frac{C_d}{K_{sd} + C_d} \right) \left(\frac{C_a}{K_{sa} + C_a} \right) \quad (2.13)$$

$$\frac{dC_a}{dt} = -k_1 * F * X \left(\frac{C_d}{K_{sd} + C_d} \right) \left(\frac{C_a}{K_{sa} + C_a} \right) - d_c * f_d * b * X \left(\frac{C_a}{K_{sa} + C_a} \right) \quad (2.14)$$

where:

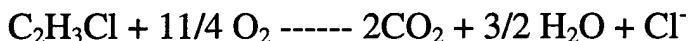
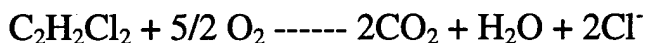
F is the stoichiometric ratio of electron acceptor to electron donor utilization for bacterial synthesis [M acceptor/M donor]

d_c is the cell decay oxygen demand [M O₂/M cells]

f_d is the fraction of cells that is biodegradable

2.3.2.2 Direct Oxidation

Some chlorinated hydrocarbons can be directly oxidized under aerobic conditions. For example, microorganisms have been shown to be capable of using VC as source of carbon and energy under aerobic conditions (Hartmans et. al., 1985; Hartmans and de Bont, 1992). It has been suggested in recent research that the isomers of DCE may degrade through direct oxidation. DCE degradation occurred rapidly within an aerobic streambed without the production of ethene, inferring oxidation to CO₂. The researchers surmised that this may have occurred by direct oxidation (Bradley and Chappelle, 1998). In direct oxidation the chlorinated solvent is oxidized to produce carbon dioxide, water and chloride ions, as shown in the reactions below (Bradley and Chapelle, 1998).



The degradation of chlorinated solvents through direct oxidation can be modeled as a first order process (Bradley and Chappelle, 1998):

$$r = \frac{dC}{dt} = -k_i * C \quad (2.14)$$

where:

k_i = first order rate constant [T⁻¹]

C = concentration of dissolved chlorinated solvent [M/L³]

2.4 Modeling

Models may be used to understand and gain insight into the various processes at work in the subsurface. As seen in the previous section, there are many interrelated processes occurring in the subsurface. A model helps to show how these processes interact, as well as to show which processes are most important in determining contaminant fate and transport. Mathematical models use equations to simulate groundwater and contaminant flow and transport in the subsurface. These equations, along with associated boundary and initial conditions, may be solved analytically or numerically. An exact analytical solution may only be obtained when the equation and initial/boundary conditions have been greatly simplified. For instance, an analytical solution could not be obtained if the model equation included nonlinearities (such as the Freundlich isotherm expressed in equation 2.5 with $n < 1$). Numerical methods, on the other hand, can be used to solve nonlinear equations with complex boundary and initial conditions. However, these methods only provide an approximate solution to the governing equations. Due to the complexity of the subsurface environment, most models that are used to simulate contaminant transport at hazardous waste sites are numerical. As part of this research is to evaluate the impact of nonlinear sorption on natural attenuation, we will only focus on numerical models. There are many numerical models that have been developed to simulate fate and transport of chemicals in the subsurface. A few of the most commonly used numerical models, which also incorporate some of the biodegradation processes of

concern in natural attenuation, are listed in Tables 2.2 and 2.3 below, and will be discussed in the following sections.

Table 2.2 Sorption Submodels

| | Sorption | | | |
|--------------|-------------|------------|--------------|------------|
| | Equilibrium | | Rate Limited | |
| Model | Linear | Non-Linear | Linear | Non-Linear |
| Bio-Redox | x | | | |
| RT3D | x | x | x | x |
| BIOPLUME III | x | | | |
| BR3D | x | x | x | x |

Table 2.3 Degradation Submodels

| | Degradation | | |
|--------------|-------------|-------|------------|
| Model | First Order | Monod | Dual Monod |
| Bio-Redox | x | x | x |
| RT3D | x | x | x |
| BIOPLUME III | x | | |
| BR3D | x | x | x |

2.4.1 Bio-Redox

BioRedox is a public domain model that can simulate coupled oxidation-reduction reactions between multiple electron acceptors and donors. It can be used to understand the influence of substrate concentrations, redox conditions, and competitive inhibition on

the natural attenuation of chlorinated solvents (Carey et al., 1999). It is capable of simulating the reductive dechlorination of chlorinated ethenes using any of the biodegradation kinetics submodels discussed earlier Table 2.3. As shown in Table 2.2, Bio-Redox can also model linear equilibrium sorption. However, Bio-Redox can not model nonlinear equilibrium sorption or either rate-limited sorption submodels. The model has the ability to simulate 3-D advection/dispersion. In addition, BioRedox can track the chloride ions that are the direct result of reductive dechlorination of chlorinated ethenes.

2.4.2 RT3D

RT3D is capable of modeling multi-species and multi-dimensional reactive transport. RT3D is able to incorporate almost any type of degradation and sorption kinetic submodels by solving a set of user specified reaction equations (Clement et al., 1999). The code is able to model 3-D advection/dispersion. As shown in Table 2.2 and 2.3, RT3D has the capability of simulating all the degradation and sorption kinetic submodels discussed previously. Unfortunately, the submodels must be specified and incorporated into RT3D by the user, and this is somewhat difficult, due to the complexity of the RT3D code.

2.4.3 BioPlume III

BIOPLUME III is a two-dimensional model that can simulate the fate and transport of chlorinated solvents. BIOPLUME III can model 2-D advection/dispersion, linear equilibrium sorption (Table 2.2), first-order decay (Table 2.3) and reactant-limited biodegradation (Wiedemeier et.al., 1999). It is based upon the method of characteristics that was developed in 1989 (Konikow and Bredehoeft, 1989).

2.4.4 BR3D

BR3D is a model developed at the Air Force Institute of Technology (Huang personal communication, 2000). BR3D is capable of modeling the degradation of chlorinated solvents through reductive dechlorination and aerobic cometabolism. It can be manipulated to model the degradation submodels shown in Table 2.3, though it is not capable of combining multiple electron acceptors and donors in oxidation-reduction processes. BR3D can simulate both equilibrium and rate-limited sorption and both linear and nonlinear isotherms. Because of its flexibility and ease of use, BR3D will be utilized in the following research.

3.0 Methodology

3.1 Overview

In this chapter, a methodology will be developed to determine if the hypothesized mechanism of rate-limited, non-linear sorption has a significant effect on the natural attenuation of PCE and TCE. The methodology is based upon the BR3D model. In the first part of this chapter a hypothetical site will be constructed and the mathematical representation of the biodegradation and sorption processes will be implemented into BR3D. In the second part of the chapter a sensitivity analysis will be conducted using BR3D to determine the effect of varying sorption parameters on the modeled natural attenuation of PCE and TCE.

3.2 Research Objectives

1. Develop a model that couples non-linear and rate-limited sorption with the relevant biodegradation processes that impact PCE and TCE fate and transport in groundwater.
2. Conduct a sensitivity analysis on the parameters used to describe the physical, chemical and biological processes that influence PCE and TCE fate and transport in groundwater.
3. Determine which parameters and processes have the largest potential effect on natural attenuation of PCE and TCE.

3.3 Site Layout and Relevant Processes

3.3.1 Site Layout

The hypothetical site being modeled will be discretized into a two-dimensional 20 by 20 grid. Each grid cell represents a 20 meter by 20 meter area, as the entire site is 400 meters by 400 meters. Each of the 400 cells is specified as shown in Figure 3.1.

| | | | | | | | | | | | | | | | | | | | |
|-----|----|----|----|----|----|----|----|----|----|----|----|----|-----|-----|-----|-----|-----|-----|----|
| IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | NF | NF | NF | NF | NF | NF | NF | AC | NF |
| IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | NF | AC | AC | AC | AC | AC | AC | AC | NF |
| NF | NF | NF | NF | NF | NF | NF | NF | NF | NF | NF | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AB* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| CS* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| CS* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| CS* | AC | AC | AC | MW | AC | AC | AC | AC | MW | AC | AC | AC | AC | MW | AC | AC | AC | AC | NF |
| CS* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| CS* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AC* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| AB* | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | AC | NF |
| NF | NF | NF | NF | NF | NF | NF | NF | NF | NF | NF | NF | NF | AC | AC | AC | AC | AC | AC | NF |
| IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | NF | AC | AC | AC | AC | AC | AC | NF |
| IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | IC | NF | AC* | AC* | AC* | AC* | AC* | AC* | NF |

Figure 3.1 Site Grid

where:

NF no flow boundary cell

AC active cell

CS contaminant source cell (pulse or constant)

MW active monitoring cell

AB electron acceptor (oxygen) and biomass source cell

IC inactive cell

* constant head boundary cell

The model assumes hydraulic conductivity is homogeneous and isotropic. As shown in Figure 3.1, a contaminant source will be placed at the west side of the grid in cells (8,1) to (12,1) (row, column). The model simulations were run using both pulse and constant source inputs. The pulse of contaminant was PCE at a concentration of 50 mg/l. The constant source contaminant was PCE at a concentration of 50 mg/l. The electron acceptor, oxygen, was placed as a constant source of 8 mg/l at cells (4,1) and (17,1). The biomass was also placed as a constant source of 0.15 mg/l at cells (4,1) and (17,1). A co-contaminant, methane, was placed as a constant source of 10 mg/l at cells (8,1) to (12,1). The co-contaminants, methane and PCE, are typically found together in landfills and fire training pits. As indicated in Figure 3.1, constant head boundaries are represented by cells (4,1) to (17,1) and cells (20,14) to (20, 19). The constant head cells (4,1) to (17,1) are set at a higher value than cells (20,14) to (20,19). Therefore the flow of groundwater is from west to south east. Monitoring wells were placed in the aquifer at cells (10,5), (10,10) and (10,15).

3.3.2 Reactions (Biodegradation and Sorption)

BR3D was chosen for its ability to simulate the anaerobic degradation of PCE as well as the anaerobic and aerobic degradation of PCE degradation daughter products. The biodegradation reactions simulated include reductive dechlorination of PCE, TCE, DCE, and VC using first-order kinetics. Aerobic cometabolic degradation of TCE, DCE, and VC was simulated using a dual Monod model. During model verification it was seen that BR3D was extremely sensitive to changes in the biodegradation parameters (see

equations 2.12, 2.13, and 2.14). The biomass, X , would grow exponentially with small changes in cell decay, yield coefficient and maximum utilization rate. After multiple simulations, a set of biodegradation parameter values was determined that led to realistic biomass concentrations. These values were held constant for the subsequent sensitivity analysis. BR3D is able to simulate first-order kinetic non-linear sorption. A non-linear, rate-limited sorption model using a Freundlich isotherm will be used to simulate sorption (equation 2.7). While sorbed, contaminant is assumed not available to be biodegraded.

3.3.3 Model Verification

Once the model was developed in FORTRAN the program was compiled using Visual FORTRAN Version 5.0. The first step in verification is to ensure that all components are being transported correctly by the model. The components include the contaminants (PCE, TCE, DCE, VC), the electron acceptor (Oxygen), the electron donor (Methane) and the biomass. The contaminant transport was checked by placing a constant source of 50 mg/l for each of the contaminants at the west side of the grid. Baseline aquifer parameters, as indicated in Tables 3.1 and 3.2, were used, with anaerobic and aerobic decay, as well as sorption of each contaminant turned off. The simulation was allowed to run and the results were recorded. As seen in Figure 3.2 the contours of each of the contaminants (PCE, TCE, DCE, VC) are the same, as would be expected. Figure 3.2 shows the length and width of the simulated aquifer, 400 meters by 400 meters. The groundwater velocity is 0.267 m/d. Therefore if the front of the plume is defined as the concentration at which it becomes half of the input (Fetter, 1993) the expected travel

distance is approximately 100 meters in one year. It can be seen from Figure 3.2 that the 25 mg/l contour is 100 meters down gradient from the source as expected.

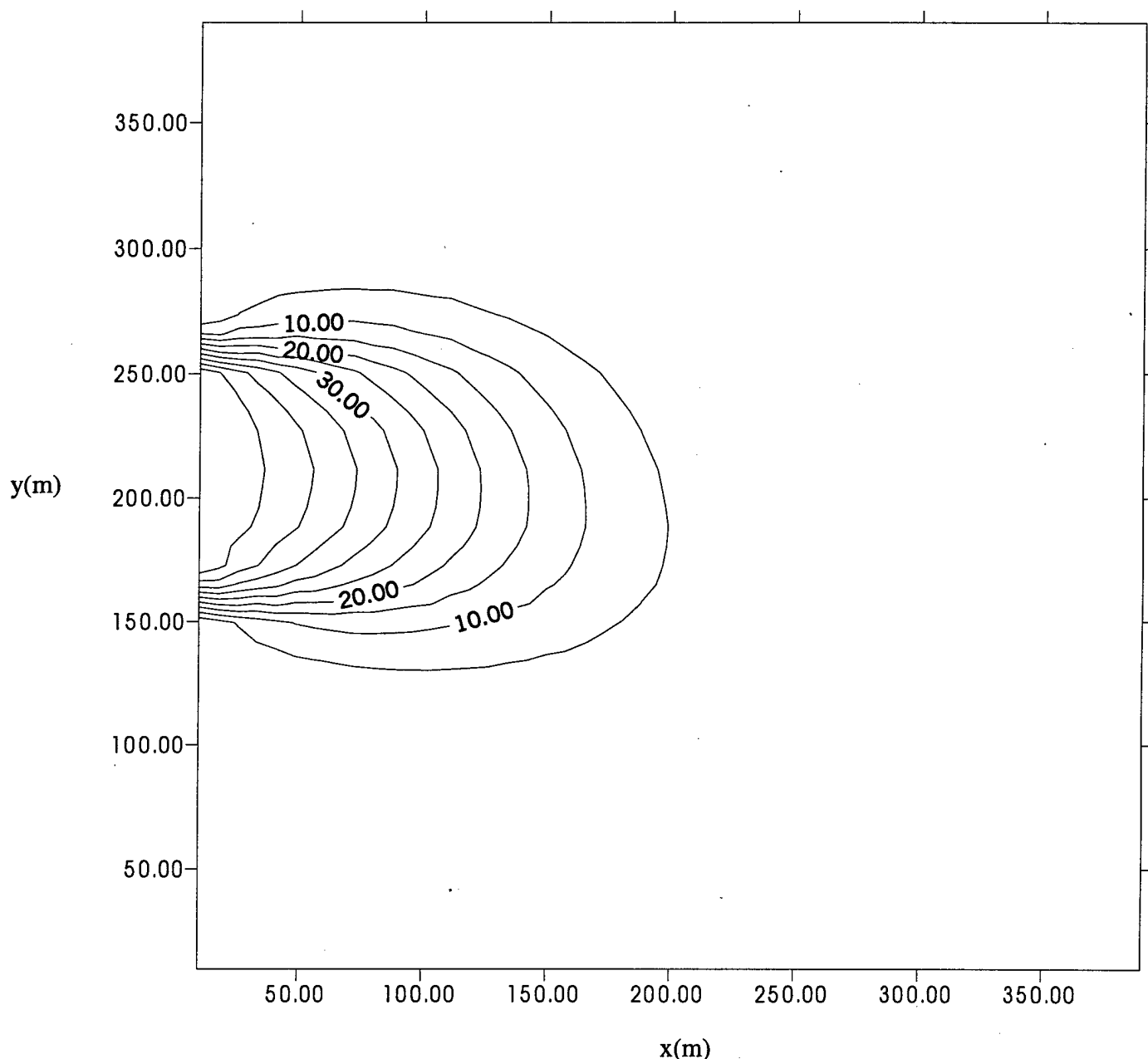


Figure 3.2 Contaminant (PCE, TCE, DCE, VC) Contours at 1 year (Advection/Dispersion Only)

The electron acceptor (oxygen) was placed as a constant source in cells (4,1) and (17,1) to represent the flow of oxygen up gradient from the contamination. This oxygen reaerates the groundwater down gradient. A monitoring well was placed at cell (10, 5) to

measure the oxygen concentration down gradient. Figure 3.3 shows the breakthrough curve of oxygen at the monitoring well. As expected, if there is no aerobic degradation, the oxygen increases to a steady state value near its input concentration. Note that the concentration of oxygen does not reach its input value of 8 mg/l because of transverse dispersion.

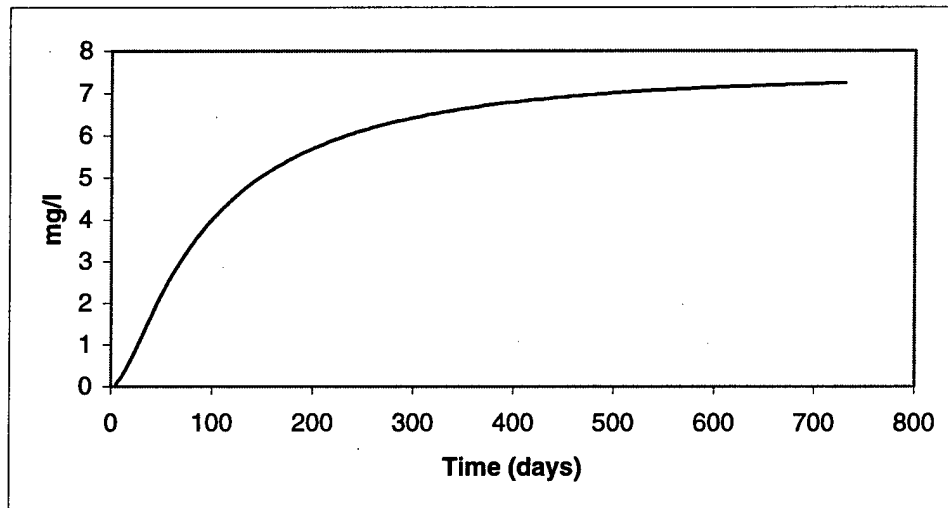


Figure 3.3 Oxygen Breakthrough Curve at Well (10,5)

The electron donor (methane) was placed as a constant source of 10 mg/l in cells (8,1) to (12,1) to represent methane production, perhaps due to methanogenesis at a landfill. A monitoring well was placed at cell (10, 5) to measure the methane concentration down gradient. If there is no degradation, the concentration of methane should reach a steady state value near its input value. This is seen in Figure 3.4. Again, note that methane concentration does not attain its source value of 10 mg/l due to transverse dispersion.

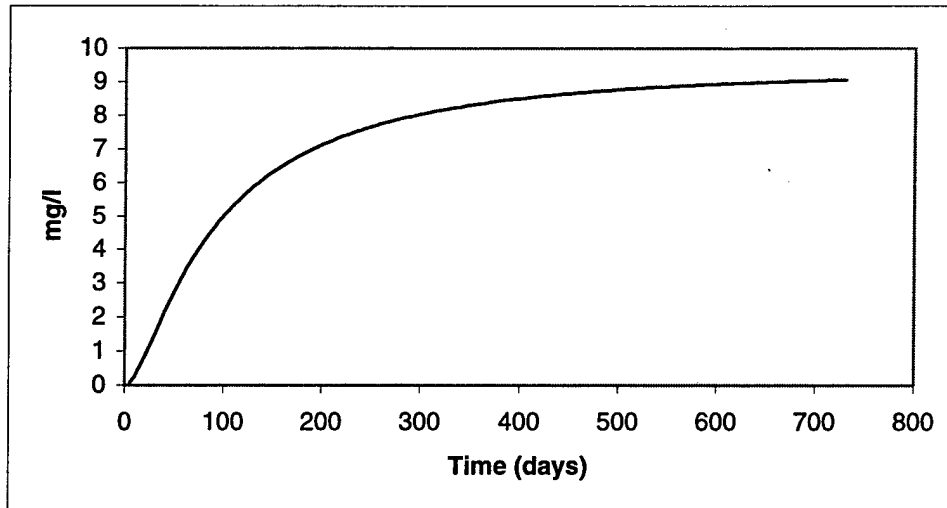


Figure 3.4 Methane Breakthrough Curve at Well (10,5)

The biomass was placed as a constant source of 0.15 mg/l in cells (4,1) and (17,1) to represent the flow of biomass from up gradient. A monitoring well was placed at cell (10, 5) down gradient to measure the biomass concentration. If there is no electron acceptor (oxygen) or donor (methane) there will be no growth or decay of the biomass and biomass should reach a steady state value near its input value. This is seen in Figure 3.5.

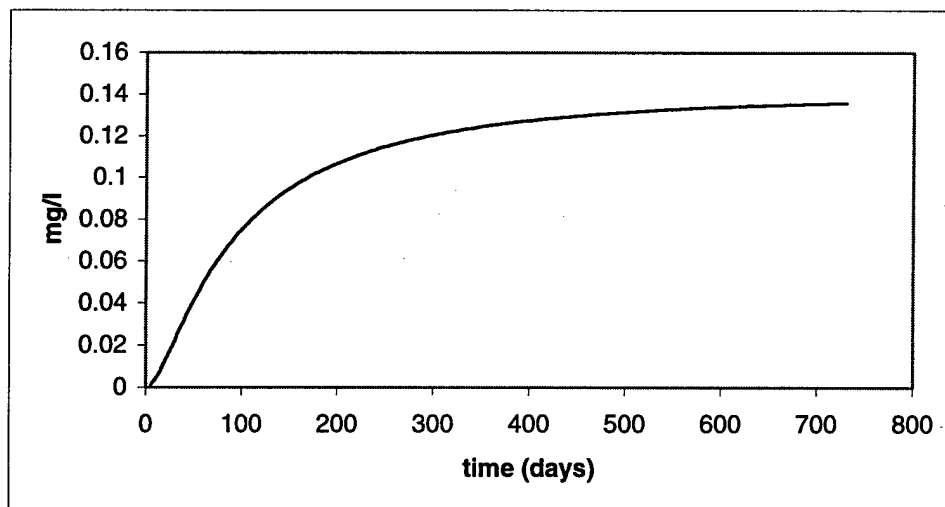


Figure 3.5 Biomass Breakthrough Curve at Well (10,5)

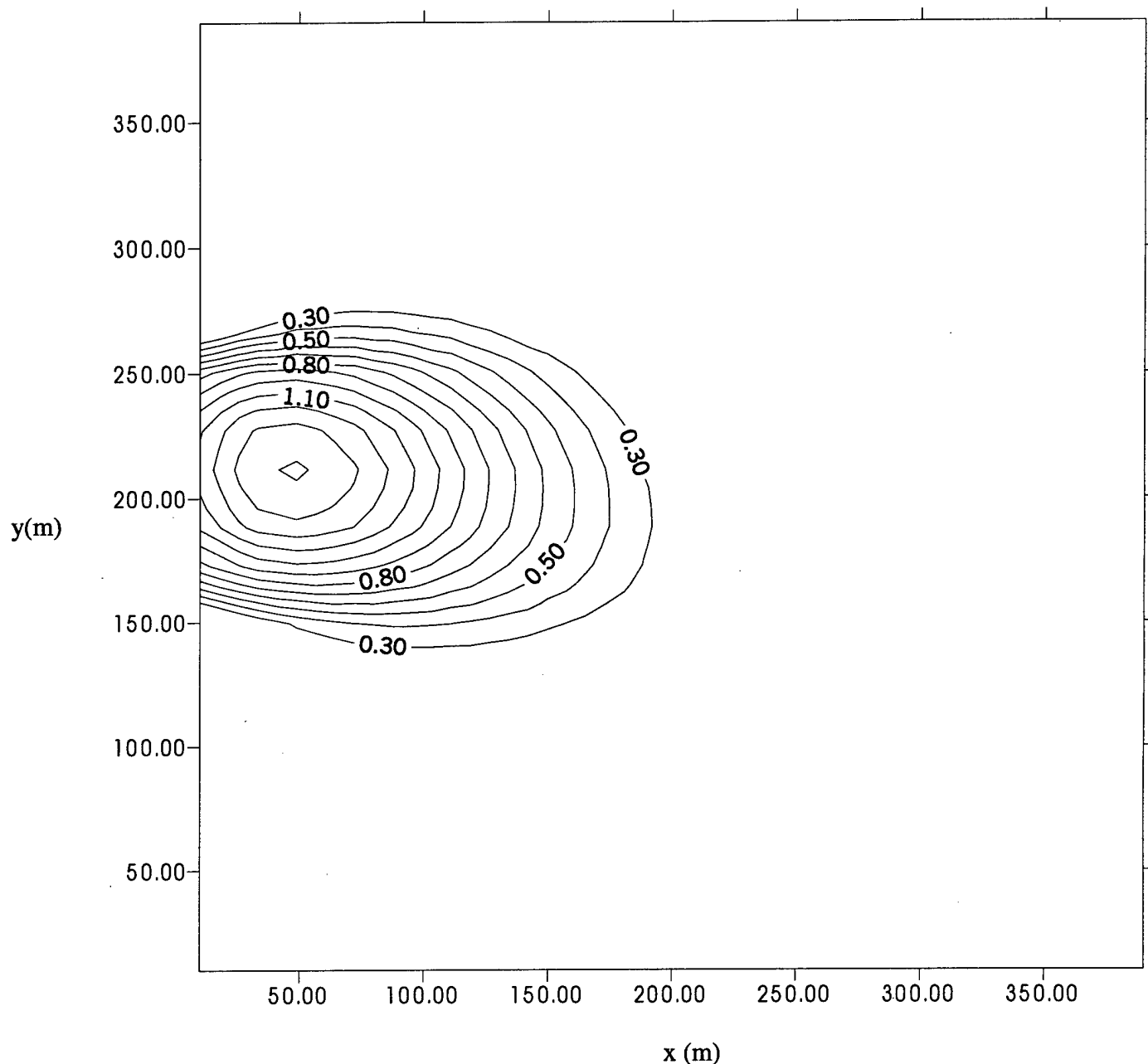


Figure 3.6 Contours (mg/l) from a Pulse Source of PCE at 2 years

Figures 3.6 through 3.10 represent the fate and transport of PCE and TCE with sorption and degradation effects. Also the figures were run with the baseline case of $n = 1$, therefore the retardation factor is 3.75. Figure 3.6 shows the concentration contours of PCE generated from a pulse source of PCE at 50 mg/l introduced into the aquifer 2 years prior. Considering retardation it is calculated that the plume should travel approximately

52 meters down gradient. The figure shows that the center of the plume is located approximately 50 meters down gradient as expected. Therefore, the model is correctly simulating the sorption of PCE in the subsurface aquifer.

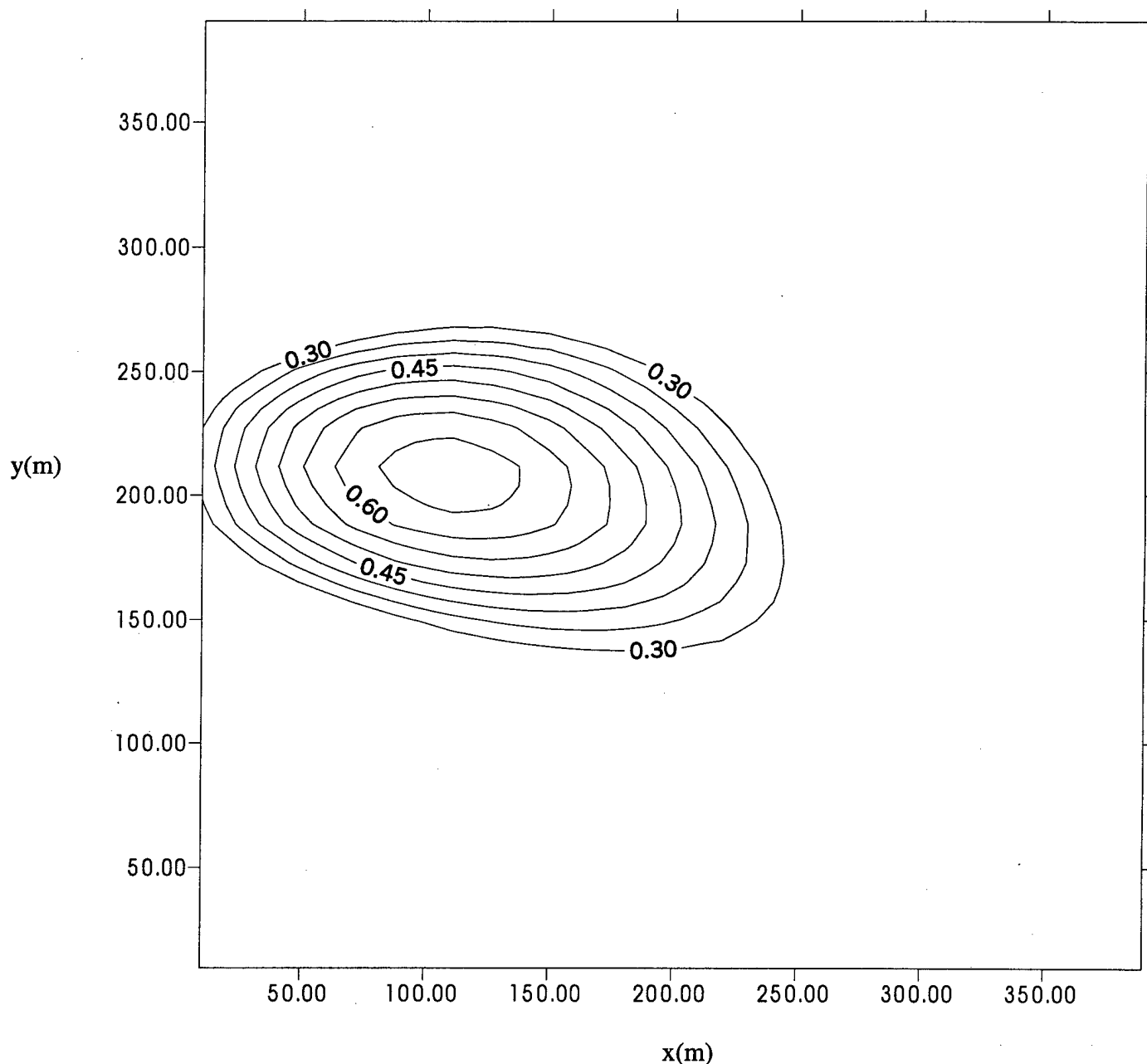


Figure 3.7 Contours (mg/l) from a Pulse Source of PCE at 5 years

Figure 3.7 shows the continued transport down gradient of PCE at time equal to 5 years.

The concentrations are lower than at 2 years due to anaerobic degradation and spreading

by dispersion. Considering retardation, it is expected that the plume should have moved 130 meters down gradient. As expected, the figure shows that the center of the plume has traveled approximately 130 meters down gradient.

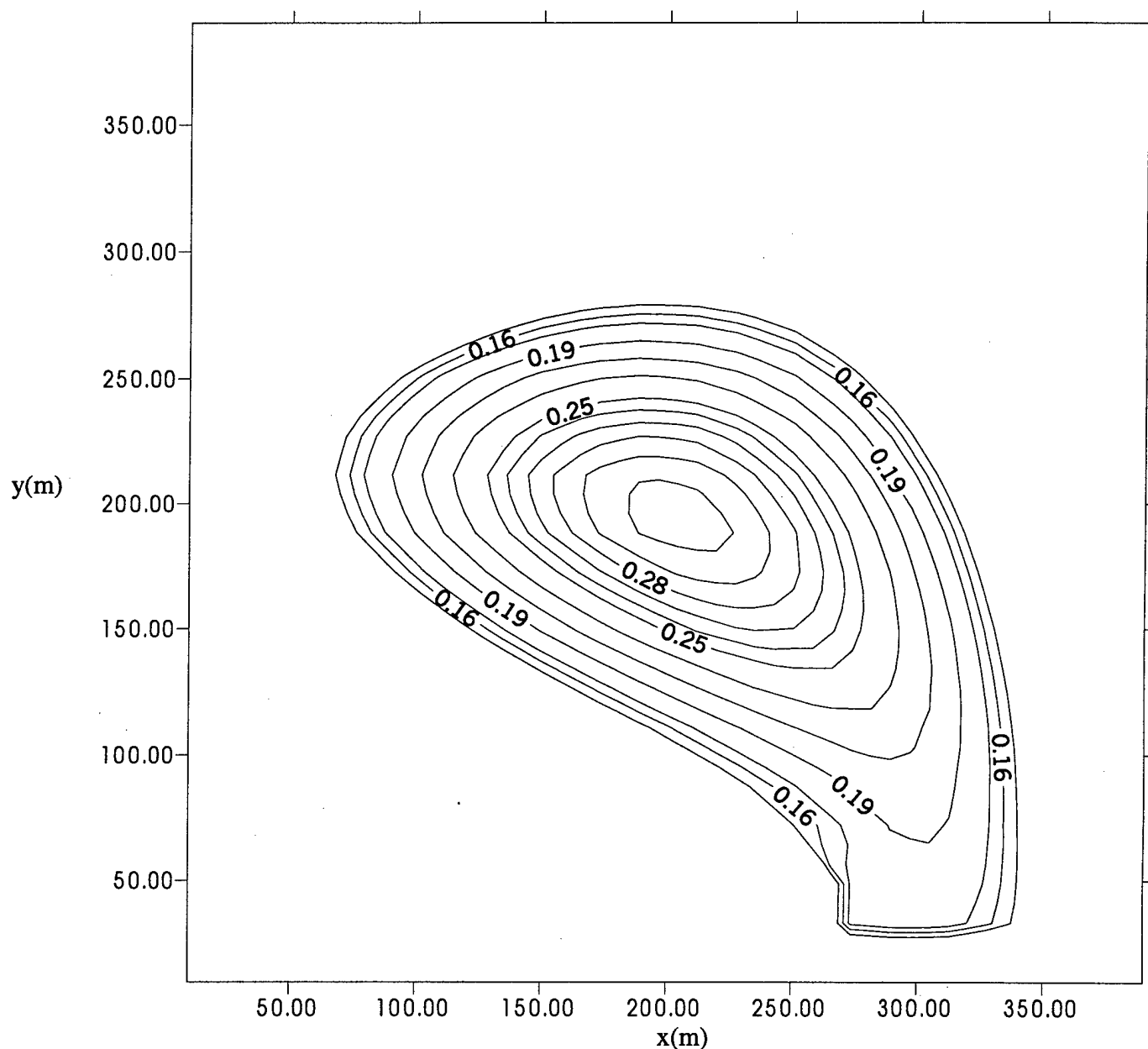


Figure 3.8 Contours (mg/l) from a Pulse Source of PCE at 10 years

Figure 3.8 shows that the contaminant, after 10 years, has continued to move down gradient. The concentrations are less than the 5 year concentrations due to anaerobic degradation and dispersion. With retardation effects, it is expected that the plume would

move 260 meters down gradient. It can be seen that the plume has moved approximately 230 meters down gradient. From these previous simulations, it appears the model, using the base case parameters, simulates advection, dispersion, and sorption effects correctly.

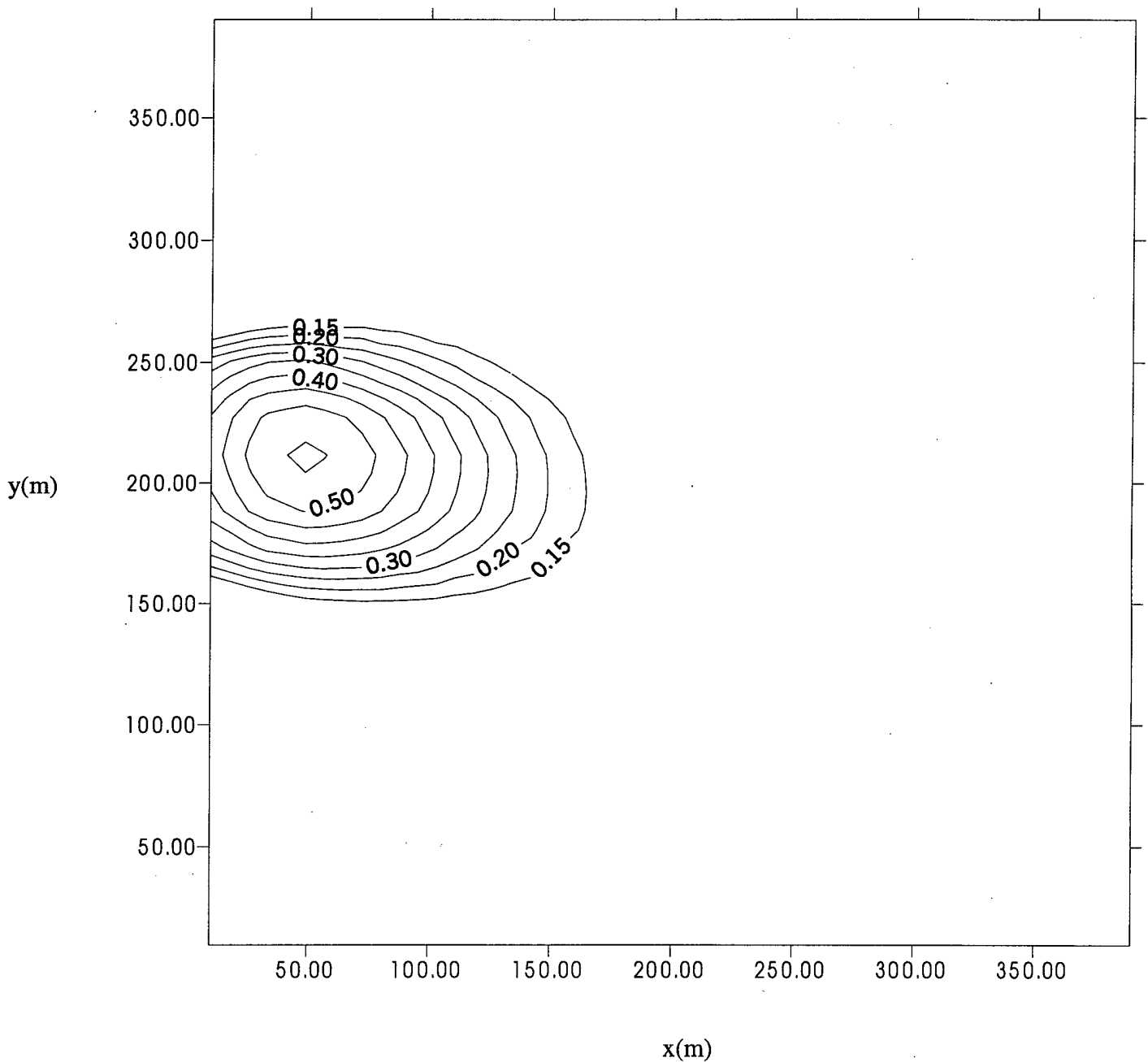


Figure 3.9 Contours (mg/l) of TCE from a Pulse Source of PCE at 2 years

Figure 3.9 shows the concentration contours of TCE at 2 years. It can be seen that the center of the plume is farther down gradient than the center of the PCE plume seen in Figure 3.6. This occurs because the PCE must degrade first before TCE can be formed.

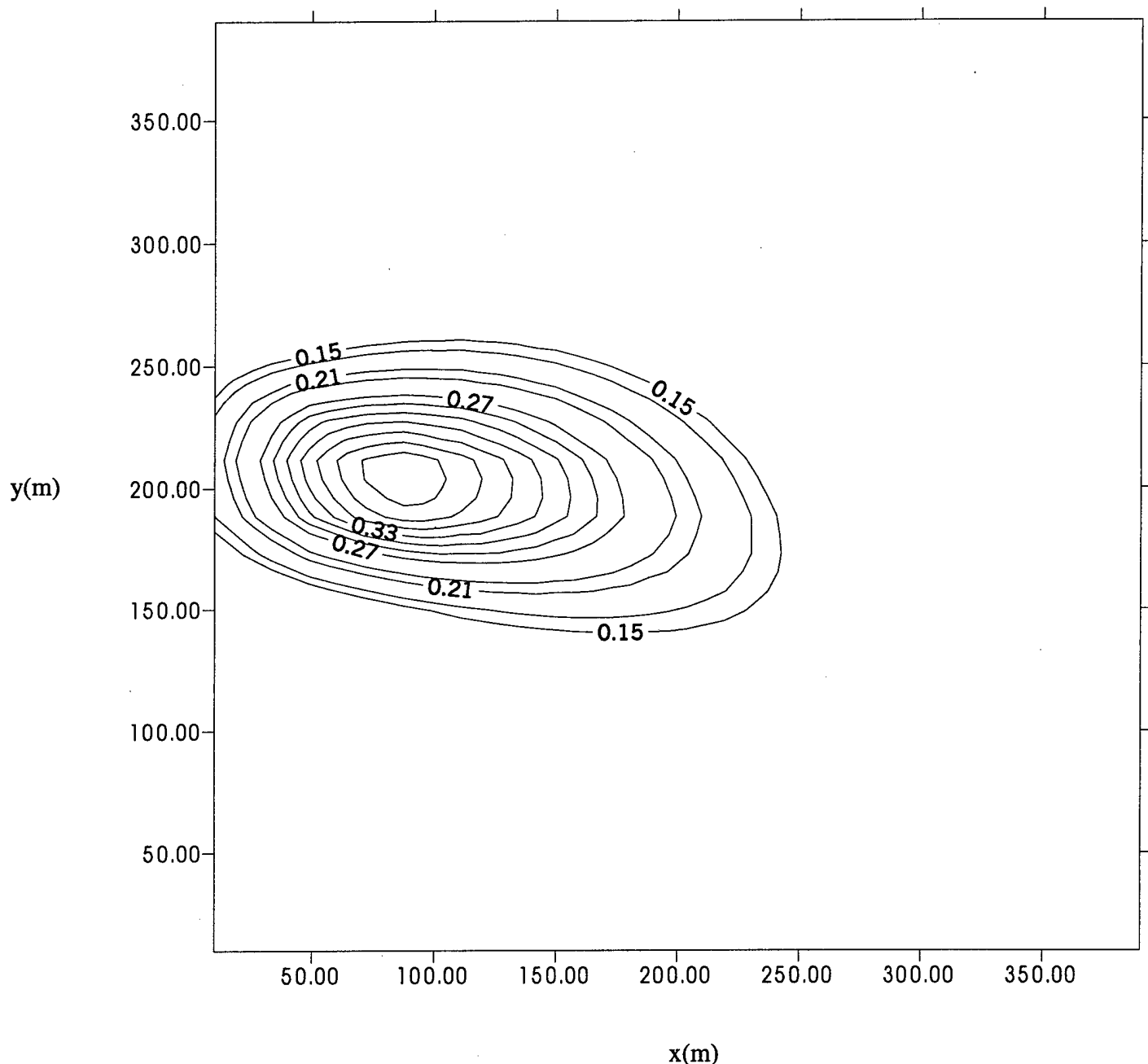


Figure 3.10 Contours (mg/l) of TCE from a Pulse Source of PCE at 5 years

Figure 3.10 shows the concentration contours of TCE after 5 years. It can be seen that the concentration levels are less than the 2 year concentration levels shown in Figure 3.9.

This is due to both anaerobic and aerobic decay, as well as dispersion. The general behavior of the plume transport simulated by the model is as expected. Therefore we have some confidence, based on these simulations, that BR3D models the fate and transport of PCE and its degradation daughter products correctly, at least in a qualitative sense.

3.4 BR3D Execution

The simulations were run following the algorithm below:

1. Define the simulation:
 - 1.1 Define the sorption variables
 - 1.2 Define the contaminant reaction variables
 - 1.3 Define observation points and simulation times
2. For each stress period:
 - 2.1 Read input file parameters
 - 2.2 Calculate flow parameters for simulation
 - 2.2.1 Calculate head parameters
 - 2.2.2 Calculate groundwater velocity
 - 2.3 For each time step
 - 2.3.1 Calculate solute transport
 - 2.3.1.1 Solve general transport equation 2.1
 - 2.3.1.2 Go to next aqueous solute, until all solutes have been transported
 - 2.3.2 Output required data
 - 2.4 Goto next timestep
3. Goto next stress period
4. End simulation

3.5 Sensitivity Analysis

The sensitivity analysis is used to determine which parameters have the largest effect on the natural attenuation of chlorinated solvents in the subsurface. The focus of this research is to determine what effect the sorption parameters have on natural attenuation. All parameters required for BR3D are listed in Table 3.1 and 3.2. The parameters in

Table 3.1 will not be varied. The parameters listed in Table 3.1 are typical values. The parameters in Table 3.2 are varied. Table 3.2 lists the baseline parameter values as well as the range over which these parameters are varied. Note that during the sensitivity analysis reported in Chapter 4, only one parameter value for one contaminant is varied at a time. All other parameters are held at the baseline value for that simulation. Table 3.2 indicates that the Freundlich adsorption constant was varied between 0.1 l/kg and 10 l/kg. This represents retardation factors varying from $R = 1.55$ to $R = 56$. The Freundlich exponent was varied between 0.1 and 1.0. This represents a range of non-linear to linear sorption isotherms. Finally the mass transfer rate was varied between 0.00001 day^{-1} and 1.0 day^{-1} . This represents a range of rate-limited to equilibrium sorption.

Breakthrough simulations were run with a single pulse of PCE being introduced at the source cells and the breakthrough curves observed at monitoring wells at cells (10,5), (10,10), and (10,15). Steady-state analyses were conducted for step inputs of PCE at the source cells. Note that daughter products are not introduced at the source cells.

Table 3.1 Parameters not varied in simulations

| Variable | Value |
|---|----------------------------|
| Bulk density of aquifer solids (ρ_b) | 1.65 kg/l |
| Groundwater Velocity (v) | 0.267 m/day |
| Longitudinal dispersivity (A_l) | 30 m |
| Transverse dispersivity (A_t) | 9 m |
| Porosity | 0.30 |
| Maximum utilization rate of cometabolism ($k_{2tce}, k_{2dce}, k_{2vc}$) | 3 day ⁻¹ |
| Contaminant half-saturation constant ($K_{stce}, K_{sdce}, K_{svc}$) | 1 mg/l |
| Electron donor/acceptor half-saturation constant (K_{sd}, K_{sa}) | 2 mg/l |
| Rate constant for first-order deactivation process (b_d) | 1 day ⁻¹ |
| Cell decay oxygen demand (d_c) (g O ₂ /g cells) | 0.5 |
| Fraction of cells that are biodegradable (f_d) | 0.9 |
| Stoichiometric rate of electron acceptor to donor utilization (F) (g acc/g don) | 2.4 |
| Cell decay coefficient (b) | 0.15 day ⁻¹ |
| Yield coefficient (Y) (g cells/g donor) | 0.5 |
| Decay yield constant for PCE (mole wt of PCE/mole wt of PCE) | 1 |
| Decay yield constant for TCE (mole wt of TCE/mole wt of PCE) | 0.79 |
| Decay yield constant for DCE (mole wt of DCE/mole wt of TCE) | 0.74 |
| Decay yield constant for VC (mole wt of VC/mole wt of DCE) | 0.64 |
| Anaerobic degradation rate constant PCE | 3.20E-04 day ⁻¹ |
| Anaerobic degradation rate constant TCE | 1.00E-04 day ⁻¹ |
| Anaerobic degradation rate constant DCE | 5.00E-05 day ⁻¹ |
| Anaerobic degradation rate constant VC | 1.00E-05 day ⁻¹ |

Table 3.2 Parameters varied in simulations

| Variable | Baseline | Range |
|--|--------------------------|----------------------------------|
| Freundlich adsorption constant ($K_{fpce}, K_{ftce}, K_{fdce}, K_{fvc}$) | 0.5 l/kg | 0.1 – 10 l/kg |
| Freundlich exponent ($n_{pce}, n_{tce}, n_{dce}, n_{vc}$) | 1 | 0.1 – 1.0 |
| Mass transfer rate ($\alpha_{pce}, \alpha_{tce}, \alpha_{dce}, \alpha_{vc}$) | 0.0036 day ⁻¹ | 0.00001 – 1.0 days ⁻¹ |

4.0 Analysis

4.1 Introduction

The results of the sensitivity analyses described in the previous chapter are reported here.

4.2 Sensitivity Analysis

4.2.1 Freundlich Adsorption Constant

The Freundlich adsorption constant, K_f , shown in equation 2.5 helps to quantify the amount of contaminant that can sorb to the aquifer material. The higher the Freundlich adsorption constant, the higher the sorbed concentration and vice versa. In this study the Freundlich adsorption constant was varied between 0.1 and 10 (l/kg). As described in the previous chapter the contaminant was introduced into the aquifer as a pulse. Therefore it is expected that the contaminant concentration at a down gradient monitoring well will reach a maximum and then eventually decrease. Based on the sorption discussion in chapter 2, it is anticipated that as the Freundlich adsorption constant decreases, contaminant breakthrough concentration at a monitoring well will increase, and arrival time at the well will decrease.

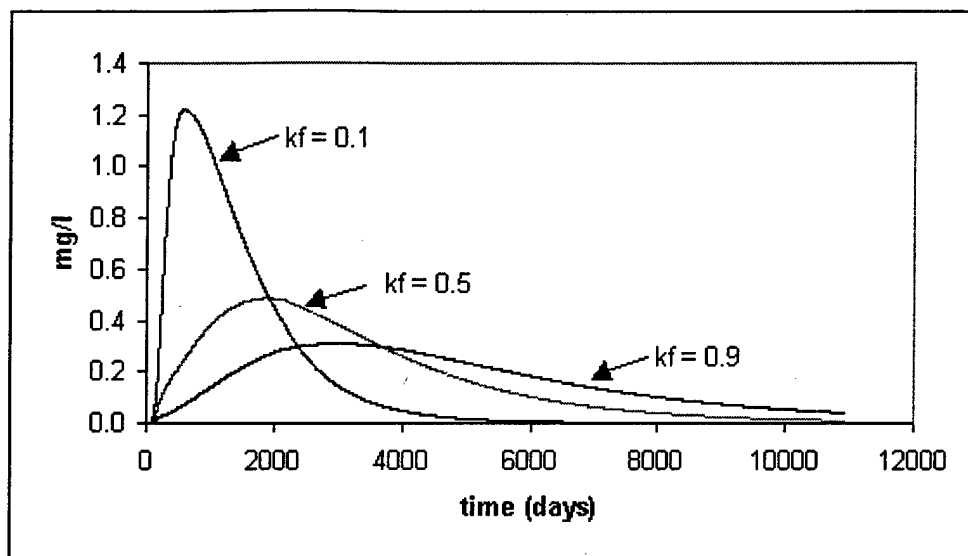


Figure 4.1 PCE Breakthrough Curve as a Function of K_f at Cell (10,10)

As shown in Figure 4.1, which depicts breakthrough at cell (10,10), 200 meters down gradient from the source cells, as the Freundlich adsorption constant increases, the time to breakthrough for PCE increases. This is as expected, as larger K_f values correspond to more sorption and retardation of the PCE. Note that when the Freundlich adsorption constant was set at 10 (l/kg), PCE transport slowed to the extent that PCE did not reach the observation cell within the 30 year simulation period. This is not unexpected, since $K_f = 10$ l/kg corresponds to $R = 56$. Thus, with a groundwater velocity of 0.267 m/d, the plume is moving at a velocity of 0.0048 m/d, and would not be expected to travel 200 m until 115 years. It is also interesting to note that as the Freundlich adsorption constant increases, the peak concentrations are dampened out. This occurs because the contaminant is in the sorbed phase a longer period of time and therefore it takes longer for all of the contaminant to flow down gradient and pass the observation cells. However, overall, the degradation will remain the same (since contaminant in the sorbed phase does not biodegrade). Hence, we would expect the areas under the breakthrough curves to be equal, since the total mass passing the observation wells should be the same,

independent of K_f . Since the length of the passing breakthrough curve increases with increasing K_f , the height of the curve will increase with decreasing K_f , in order that the areas remain equal. The breakthrough curves depicted in Figure 4.1 show this expected behavior with changes in K_f .

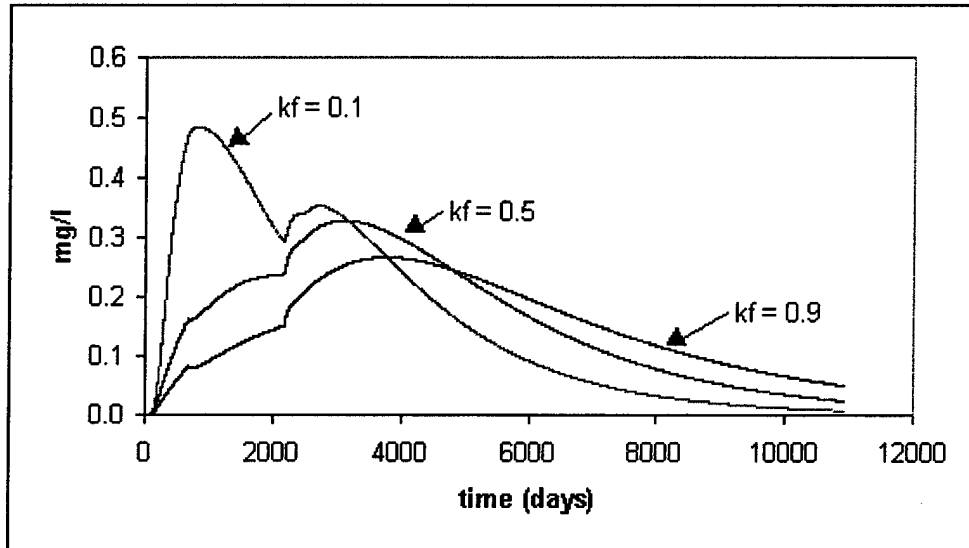


Figure 4.2 TCE Breakthrough Curve as a Function of K_f at Cell (10,10)

As discussed in section 2.3.1.1, TCE is formed from the reductive dechlorination of PCE. Therefore as PCE is degraded, the TCE concentration will increase. As the TCE Freundlich adsorption constants get larger, TCE transport is slowed and TCE breakthrough is shifted to the right, as depicted in Figure 4.2. An interesting result is seen when the Freundlich adsorption constant is set to 0.1 (l/kg). This double peak behavior of the breakthrough curve is apparently due to the changing anaerobic and aerobic zones within the aquifer.

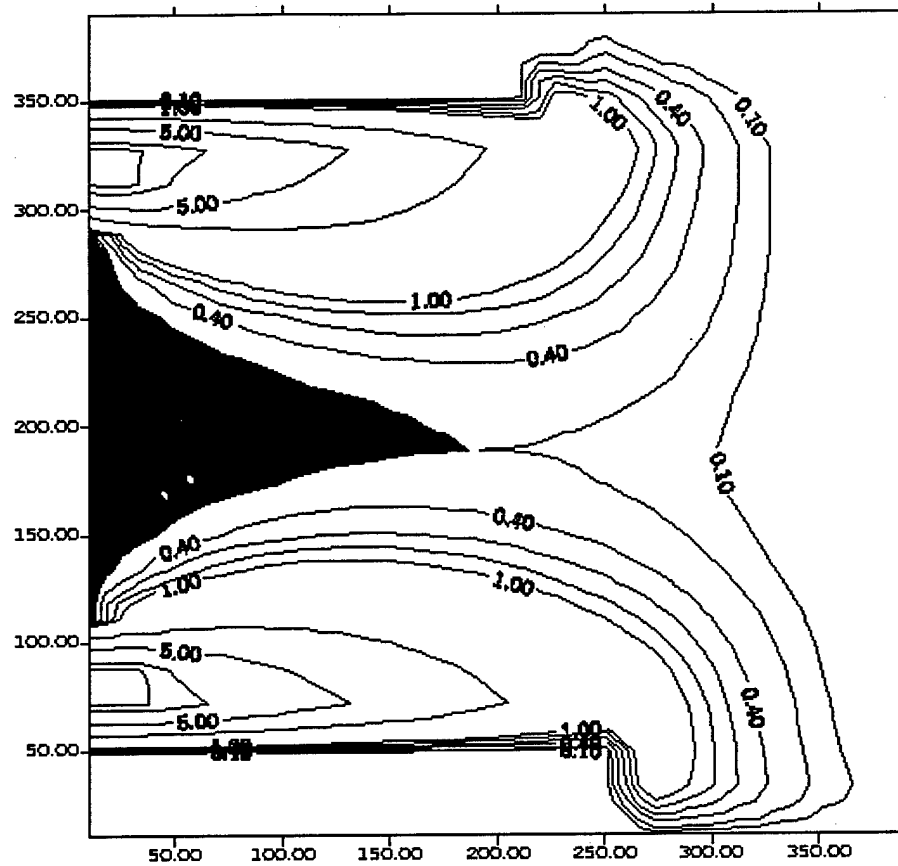


Figure 4.3 Spatial Contours of Oxygen at 2 years

As shown in Figure 4.3, the area within the shaded region is anaerobic. In that region, the PCE anaerobically degrades and forms TCE. This represents the increase in TCE from time zero to 800 days.

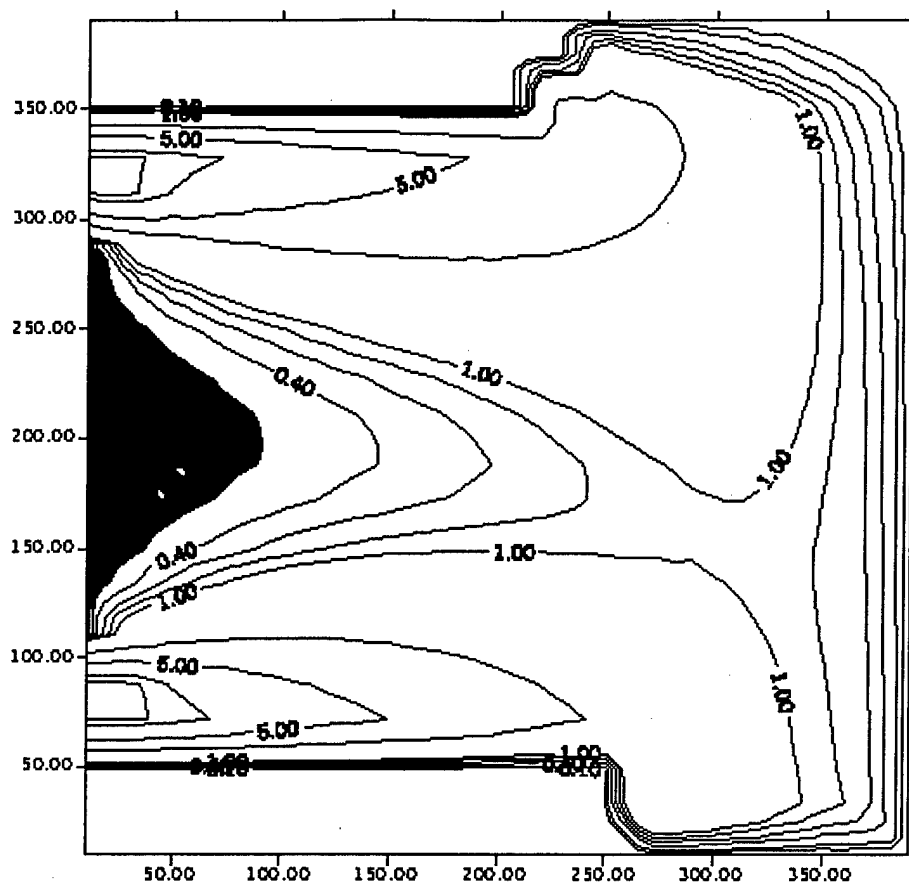


Figure 4.4 Spatial Contours of Oxygen at 4.5 years

Then as seen by comparing Figures 4.3 and 4.4 the anaerobic area shrinks between 2 and 4.5 years and the aquifer becomes more aerobic. As the aquifer becomes more aerobic, production of TCE by PCE degradation slows. However, TCE degradation continues, via aerobic cometabolism. This explains the decrease in TCE concentration up to about 2000 days (5.5 years).

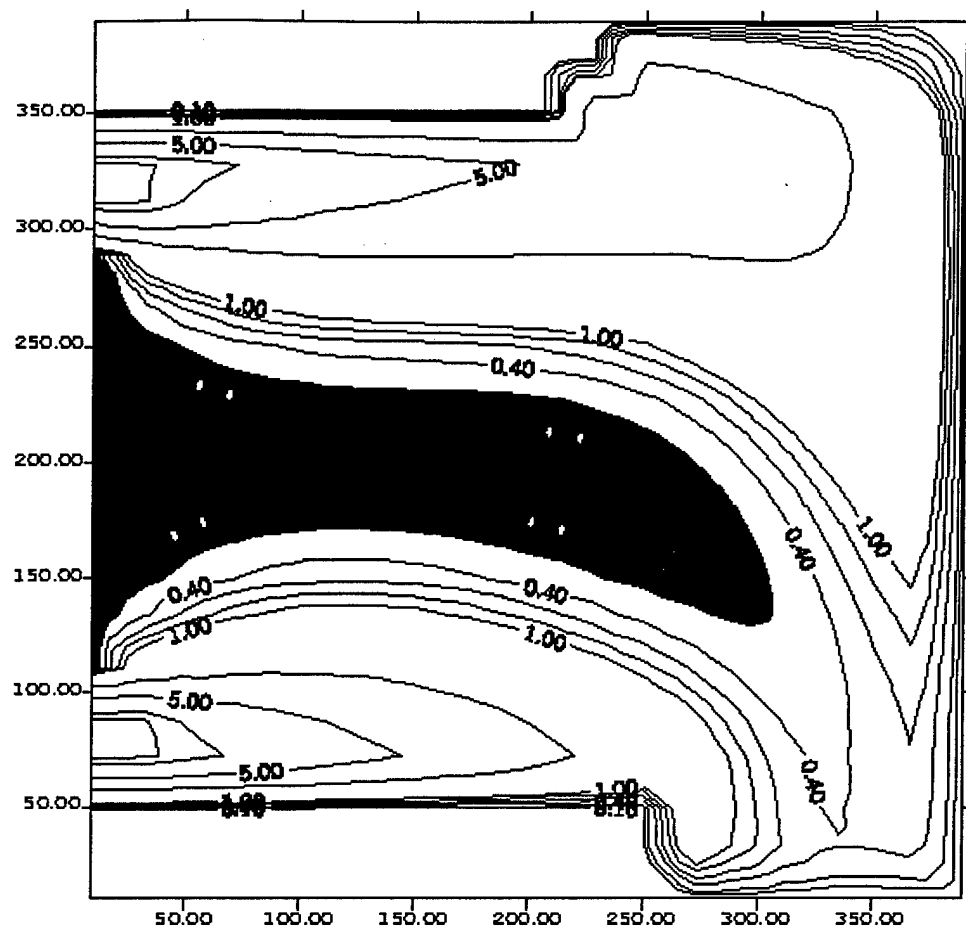


Figure 4.5 Spatial Contours of Oxygen at 8 years

Comparison of Figures 4.4 and 4.5 shows the aquifer becoming more anaerobic from 4.5 to 8 years. In this period, TCE production from anaerobic degradation of PCE begins again which explains the rise in TCE. Ultimately, the pulses of PCE and TCE pass the monitoring well and the concentrations decrease. The aerobic/anaerobic zones of the aquifer are formed by the complex interactions of the biomass, electron acceptor and electron donor. The general trends displayed by the TCE in Figure 4.2 are also representative of the behavior of the TCE degradation daughter products, DCE and VC.

4.2.2 Freundlich Exponent

The Freundlich exponent helps to explain the nonlinearity associated with the sorption process. As seen in Figure 4.6, as the Freundlich exponent decreased the breakthrough curves shifted to the left. This occurs because at low values of n , low concentrations are retarded more than higher concentrations. Therefore, breakthrough curves will exhibit sharp fronts and long tailing. The sharp fronts occur because the low concentration levels of contaminant that disperse ahead of the main wave of contaminant are retarded more than the main wave, allowing the wave to “catch up” to the leading edge. Long tailing occurs because low concentrations of contaminant behind the main wave get retarded even further and lag behind. The sharp breakthrough curves and tailing can be seen in the low n simulation in Figures 4.6 and 4.7.

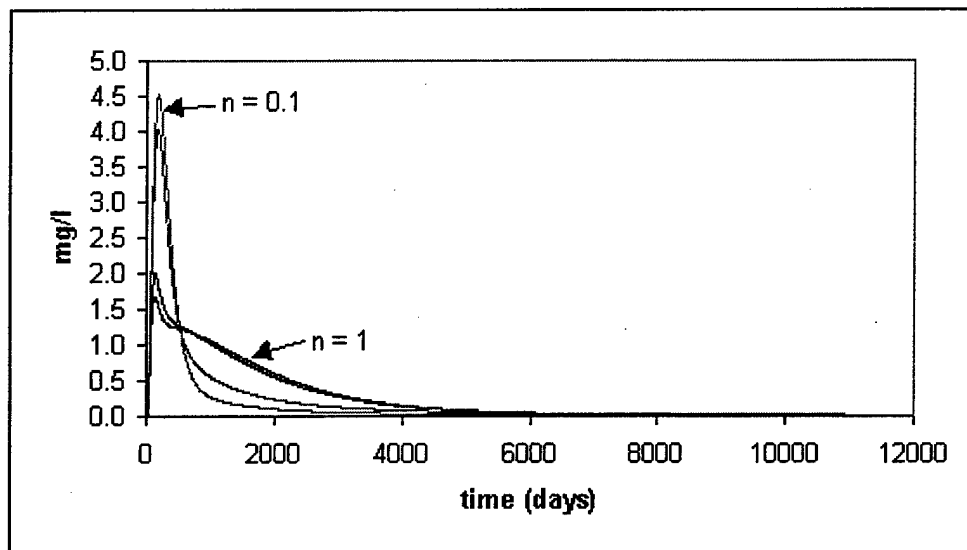


Figure 4.6 PCE Breakthrough Curve as a Function of n at Cell (10,5)

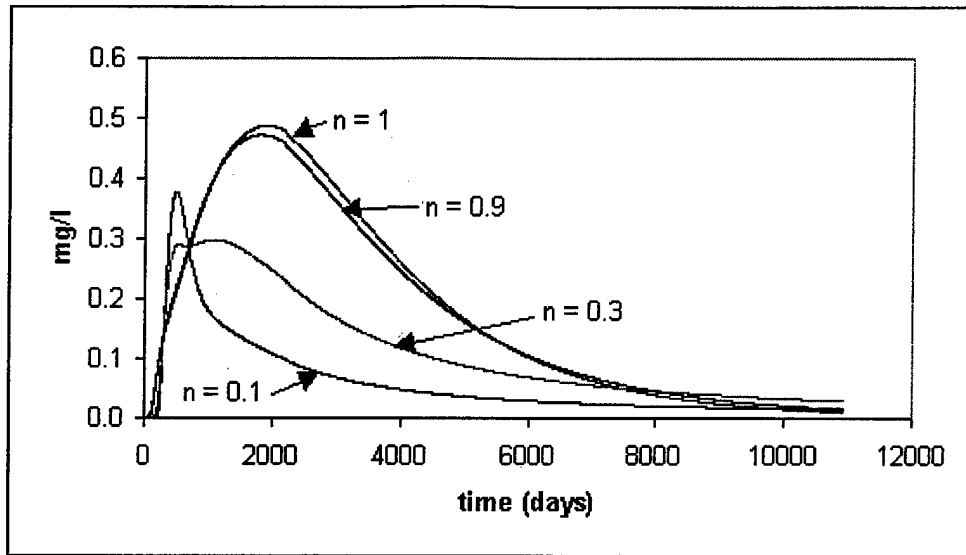


Figure 4.7 PCE Breakthrough Curve as a Function of n at Cell (10,10)

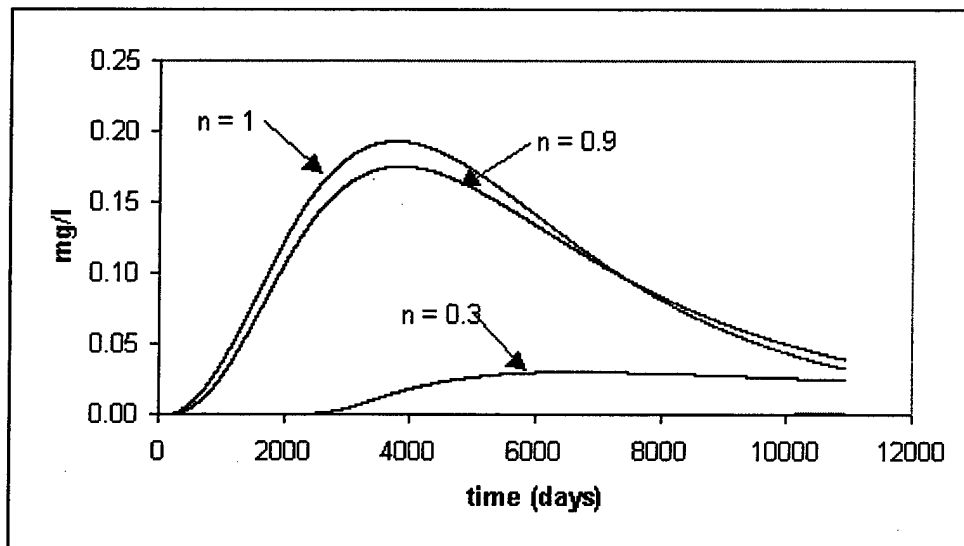


Figure 4.8 PCE Breakthrough Curve as a Function of n at Cell (10,15)

The sharpening of breakthrough curves is not seen for PCE at observation point (10,15).

As seen in Figure 4.8, the breakthrough curves are shifted to the right for smaller Freundlich exponent values. This occurs because the anaerobic degradation has had time to degrade the contaminant. Since the anaerobic degradation was modeled as a first-order process, the larger concentrations at cell (10,5) associated with low values of n lead to more degradation.

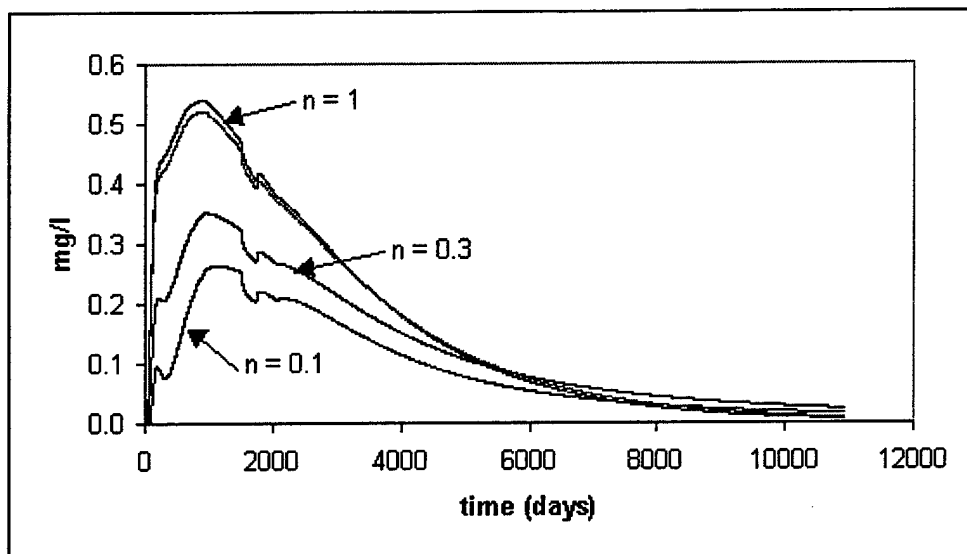


Figure 4.9 TCE Breakthrough Curve as a Function of n at Cell (10,5)

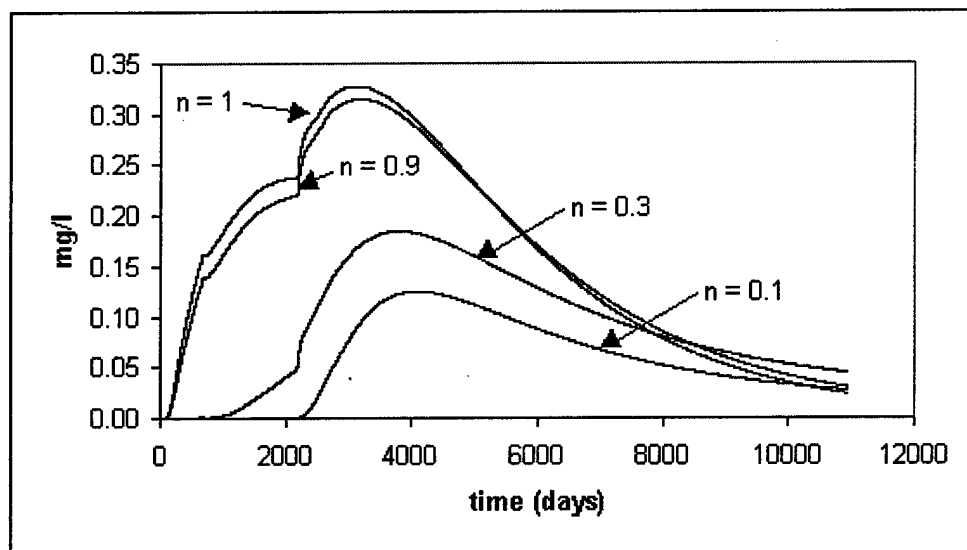


Figure 4.10 TCE Breakthrough Curve as a Function of n at Cell (10,10)

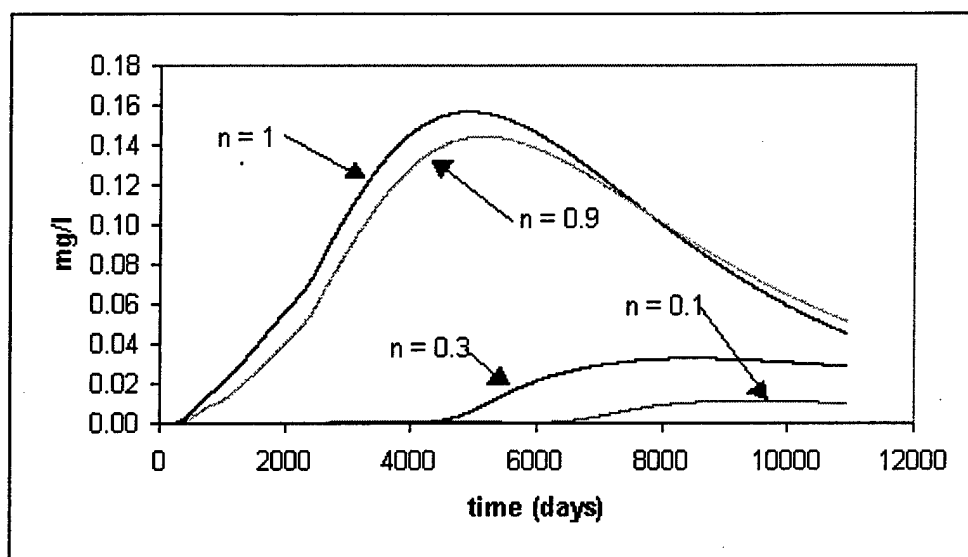


Figure 4.11 TCE Breakthrough Curve as a Function of n at Cell (10,15)

The parameters used to simulate Figures 4.9, 4.10, and 4.11 are all baseline parameters except for varying the Freundlich exponent for TCE. As seen in Figures 4.9, 4.10, and 4.11, the general trend for TCE is for the breakthrough concentration to decrease and the arrival time to increase as the Freundlich exponent is decreased. Since TCE is produced from PCE degradation, at low n , the low TCE concentrations initially produced are strongly sorbed, leading to increased retardation and breakthrough time for the low n simulations. Also notice, when comparing Figures 4.9 and 4.10, that the peak concentration at observation cell (10,5) is less than at (10,10). This occurs because the PCE must degrade first to form TCE. The maximum production of TCE does not occur until after observation cell (10,5). This behavior is also observed for the TCE degradation daughter products, DCE and VC.

4.2.3 Sensitivity Analysis of Downgradient Steady-State Concentrations

Table 4.1 shows the steady-state contaminant concentrations at observation cells that are 100 m, 200 m, and 300 m down gradient from the contaminant source for a constant input

of 50 mg/l PCE. At each of the observation points the PCE reached higher concentrations than the daughter contaminants. As expected, for PCE, the further down gradient wells are at lower concentrations than wells closer to the source. Of course, this occurs because there is no production of PCE down gradient of the source, so the further PCE travels, the more it degrades and disperses. On the other hand, note that steady state concentrations of some of the daughter products (TCE and DCE) reach a peak at the intermediate observation well. This is because these daughter products are formed during transport, and the peak location is a function of the particular advection and degradation/production rates specified in the baseline parameters.

Table 4.1 Steady State Concentration Levels

| Solute | Observation Cell (100 m downgradient) | Observation Cell (200 m downgradient) | Observation Cell (300 m downgradient) |
|--------|--|--|--|
| PCE | 40 mg/l | 26.0 mg/l | 17.0 mg/l |
| TCE | 8 mg/l | 11.0 mg/l | 4.0 mg/l |
| DCE | 0.37 mg/l | 0.75 mg/l | 0.2 mg/l |
| VC | 0.008 mg/l | 0.02 mg/l | 0.006 mg/l |

4.2.4 Mass Transfer Rate

As seen in Figure 4.12, the mass transfer rate had a large effect on the breakthrough curve for PCE. This behavior is even more pronounced for the daughter products of PCE degradation, such as TCE (Figure 4.13).

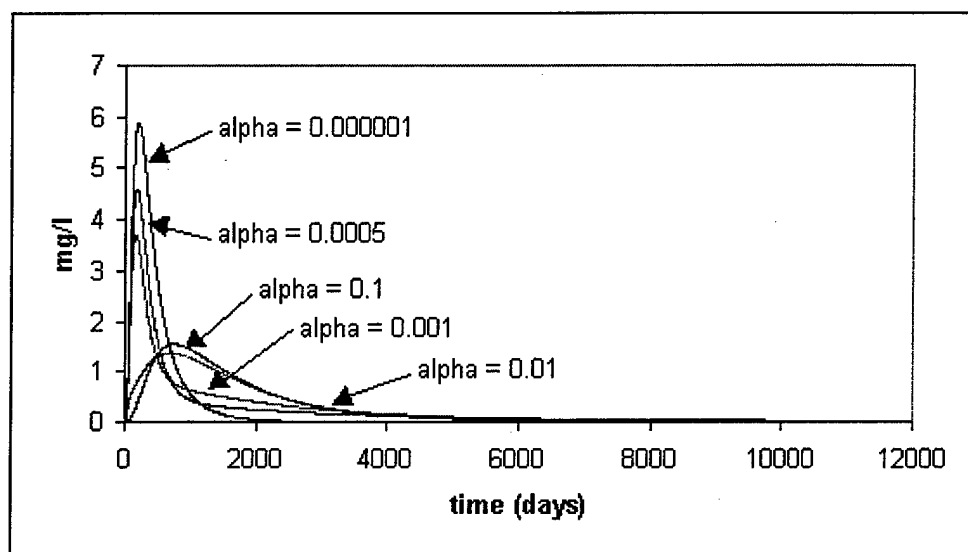


Figure 4.12 PCE Breakthrough Curve as a Function of α at Cell (10,5)
Note: Units of α are days⁻¹

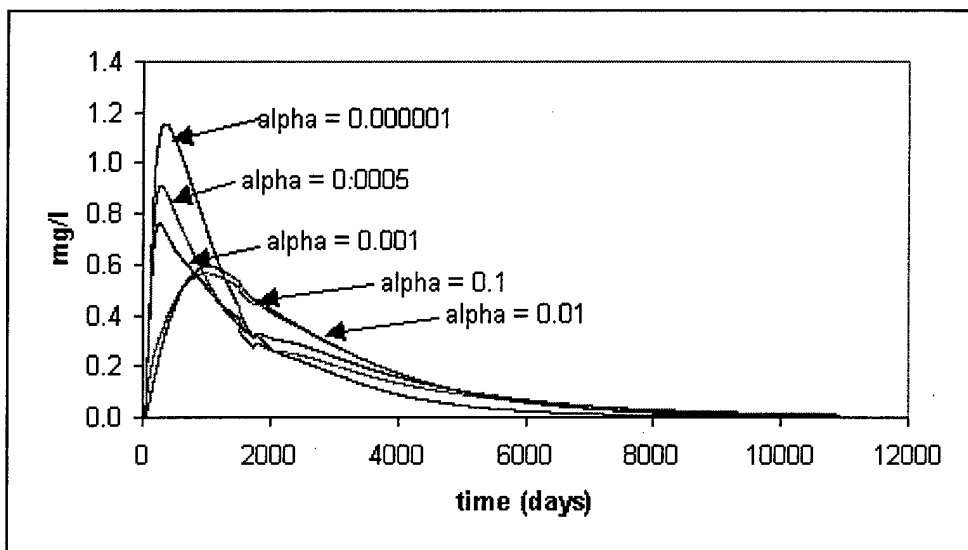


Figure 4.13 TCE Breakthrough Curve as a Function of α at Cell (10,5)
Note: Units of α are days⁻¹

Figures 4.12 and 4.13 show that small mass transfer rates lead to sharp breakthrough curves with tailing. The breakthrough curves become more symmetric as the mass transfer rate increases. This occurs because, at extremely small mass transfer rates, the contaminant is not sorbed to the soil and flows with the groundwater. However, the contaminant that does sorb tends to remain sorbed and creates a breakthrough curve tail.

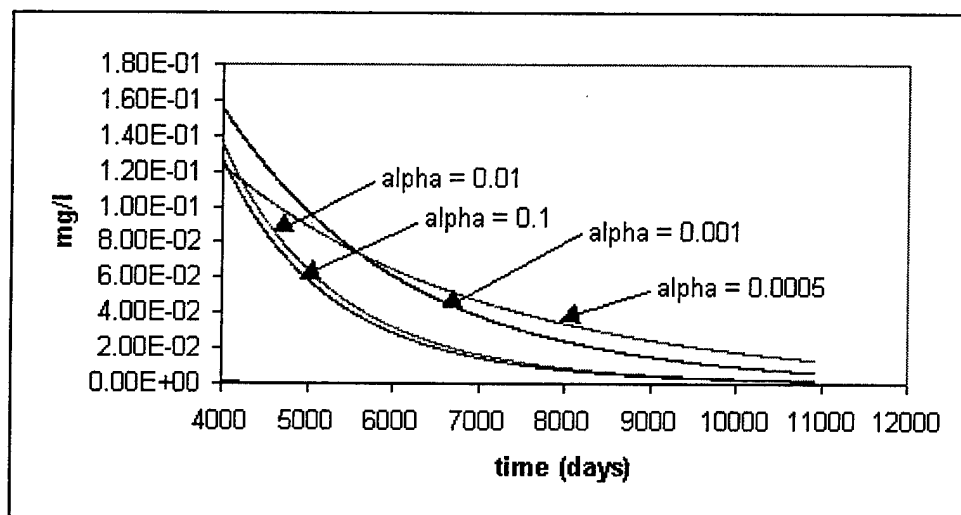


Figure 4.14 PCE Breakthrough Curve Tail as a Function of α at Cell (10,5)
Note: Units of α are days^{-1}

As seen in Figure 4.14, simulations at the smaller mass transfer rates have more pronounced tailing than the higher mass transfer rate simulations. As discussed in Section 2.2.3.2.2, the ratio of the advection and diffusion timescales determines the relative effect of the mass transfer rate. For PCE at well (10,5) a mass transfer rate of 0.0001 days^{-1} resulted in an advective/diffusive timescale (see equation 2.8) ratio close to 0.1 which would be expected to show the largest effect of rate-limited sorption (Goltz and Oxley, 1991). Note that the curves for $\alpha = 0.01 \text{ days}^{-1}$ and $\alpha = 0.1 \text{ days}^{-1}$ are similar, indicating that for values of α greater than about 0.1 days^{-1} , sorption is nearly at

equilibrium. The general trend shown for PCE and TCE is representative of the behavior for the degradation daughter products, DCE and VC.

5.0 Conclusions

5.1 Summary

In this thesis, a model, BR3D, was developed to describe the natural attenuation of chlorinated ethenes in an aquifer. The model incorporated anaerobic and aerobic degradation zones. The chlorinated solvents degraded through reductive dechlorination in the anaerobic zone, simulated using a first-order decay model. PCE daughter products also degraded through cometabolism in the aerobic zone simulated using dual Monod kinetics. The model also incorporated first-order sorption kinetics coupled with a Freundlich isotherm. Using BR3D, a sensitivity analysis was performed to ascertain the effect of sorption on the natural attenuation of chlorinated solvents.

5.2 Sensitivity Analysis

Initially it was found that the model was extremely sensitive to the change in biomass growth and decay parameters. This can make it extremely difficult to apply the model to real world situations. The decay and growth of biomass is extremely difficult to measure in the field and it is difficult to extrapolate the data collected from laboratory results to accurately model what is occurring in subsurface aquifers.

The Freundlich adsorption constant (K_f) had an effect on chlorinated ethenes fate and transport. The general effect is for the higher Freundlich coefficients to slow advective transport through retardation. This phenomenon is expected. As the extent of sorption for each contaminant increases, the time to breakthrough will also increase. However, because contaminant is assumed to not biodegrade in the sorbed phase, the Freundlich

adsorption constant did not affect overall biodegradation, since both physical transport and biodegradation are slowed equally. Therefore large Freundlich adsorption constants lead to lower concentrations for a longer period of time at a well.

The Freundlich exponent significantly affects the contaminant breakthrough curves. The breakthrough curves exhibit sharp fronts and long tailing with low Freundlich exponent values. Smaller Freundlich exponents lead to higher sorption for low contaminant concentrations which corresponds to tailing and longer remediation times. Freundlich exponents close to unity result in relatively symmetric breakthrough curves. Therefore, lower Freundlich exponents lead to higher concentrations for a longer period of time at a well.

It was seen that the steady-state concentrations depend on the parameter values. The first-order decay rates and the rate and extent of cometabolic degradation will influence the steady-state concentrations. The influence of these parameters on steady state concentration was not explored in this thesis, but could be the subject of future research. In the current study, the peak steady-state concentrations of particular contaminants were found to occur at different locations in the aquifer.

It was determined that the mass transfer rate caused large changes in the breakthrough curves for the chlorinated ethenes. The result is that for extremely small mass transfer rates, the contaminant exhibited sharp breakthrough and extensive tailing. Small mass transfer rates mean that initially, contaminant may be advected without being sorbed.

However, those molecules of contaminant that are sorbed will remain on the subsurface aquifer material for a long time and only slowly desorb back into the aqueous phase.

This explains the sharp breakthrough and tailing observed when the mass transfer rates are low resulting in higher concentrations for a longer period of time than for higher mass transfer rates. The ultimate impact of rate-limited sorption, especially on wells relatively close to the source, is that the contaminant will reach the wells faster and remain at the wells for a longer period of time, at higher concentrations than would be observed if sorption were not rate-limited.

The model, BR3D, was capable of simulating the effect of non-linear and rate-limited sorption on natural attenuation of chlorinated solvents. It showed that both non-linear and rate-limited sorption had large effects on the concentrations of PCE and its degradation daughter products. The model could help site managers determine if natural attenuation will meet time and concentration objectives for contaminant cleanup. Based on the results of this study, it appears that both non-linear and rate-limited sorption have similar effects on chlorinated ethene fate and transport. Both phenomena result in earlier contaminant arrival and longer contaminant persistence at a well than would be observed if sorption was linear and rapid. Site managers should consider these phenomena when making decisions on the applicability of natural attenuation.

5.3 Further Research

1. Incorporate multiple electron acceptors into the model perhaps using Bio-Redox. As discussed in section 2.4.4, BR3D does not allow for multiple electron acceptors.

Therefore, incorporating multiple electron acceptors into the model may allow for more accurate simulation of the subsurface aquifer.

2. Explore the growth, decay, and transport of biomass within the subsurface aquifer.

As discussed in section 3.3.2, model results were extremely sensitive to changes in the biomass parameters. Therefore it is necessary to explore this area and develop more accurate models of biomass growth, decay, and transport.

3. Validate the model with field data. As discussed in section 3.3.3, BR3D, was only qualitatively verified. Model validation is a prerequisite if we hope to use the model in determining the impact of natural attenuation on chlorinated ethene fate.
4. Conduct a quantitative study using BR3D. Determine which parameters lead to the largest mass degraded and the reduction of toxicity. Determine what parameters lead to minimized risk to human health.

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